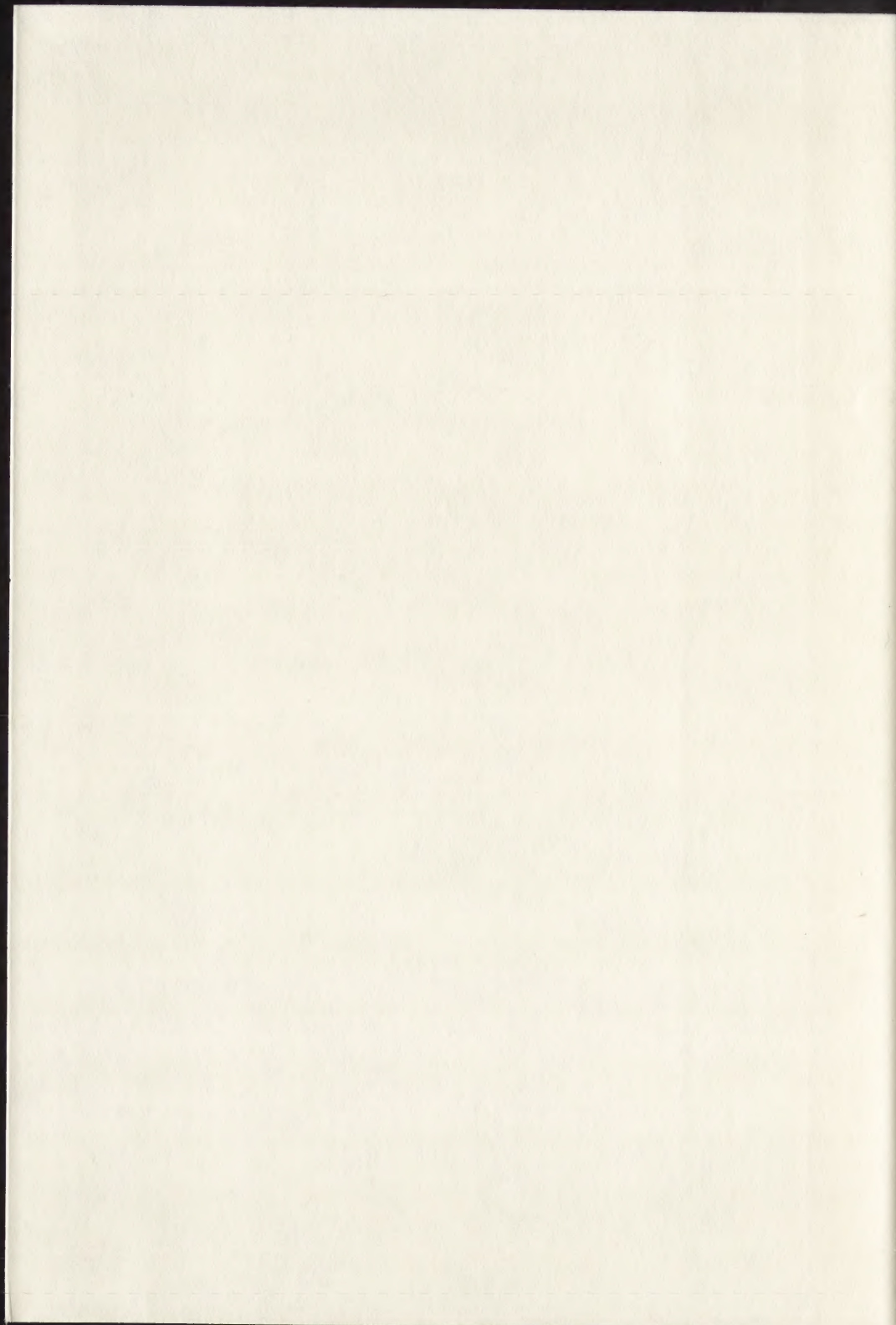


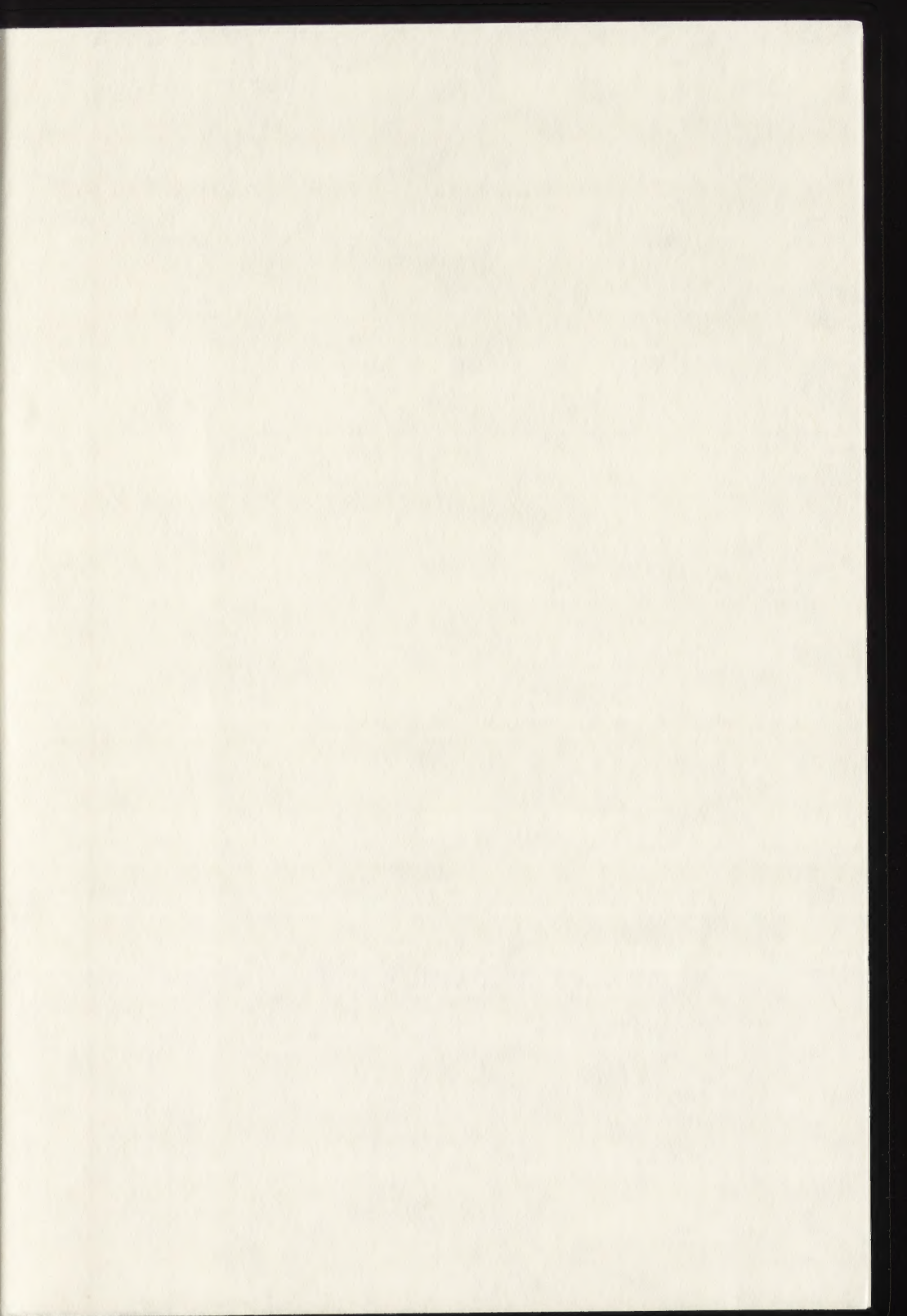
THE GETTY CENTER LIBRARY



Why ask for the moon
When we have the stars?









GRAPHIC AND PHOTOGRAPHIC DOCUMENTS

Coordinator: F. Flieder (France)

Members : O.P.Agrawal (India)
 C. Chahine (France)
 J.H.Hofenk-de Graaff (Netherlands)
 B. Kastaly (Hungary)
 R. Kowalik (Poland)
 J. Nyuksha (USSR)
 V. Radosavljevic (Yugoslavia)
 W.G.Roelofs (Netherlands)
 T. Stambolov (Netherlands)
 L. Stanojlovic (Canada)
 J.L.Stone (USA)
 L. Tchernikova (USSR)
 V. Viñas Torner (Spain)
 A. Zappala (Italy)

Programme 1978-1981

1. Mise au point de "traitement de masse" pour la désacidification et le blanchiment des papiers.
2. Etude des polymères pouvant être utilisés pour fixer les tracés.
3. Etude de l'effet de la pollution atmosphérique sur les cuirs et les parchemins.
4. Etude de la couche picturale des enluminures serbes datant du XIIe au XVIIIe siècle.
5. Analyse des encres et des enluminures par la chromatographie en phase vapeur et la chromatographie liquide haute performance.
6. Mise au point des conditions de conservation d'archivage de longue durée des matériaux photographiques noir et blanc et couleur.
 La restauration des parchemins gorgés d'eau et des parchemins acides.
8. La restauration des papiers muraux, des journaux et des périodiques.

CONS.

N

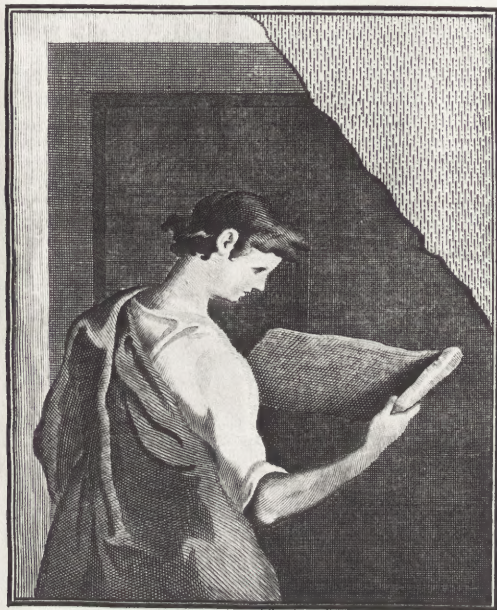
8554.5

I61

C73

1981

v.3



THE J. PAUL GETTY MUSEUM LIBRARY

GROUPE DE TRAVAIL DOCUMENTS GRAPHIQUES ET PHOTOGRAPHIQUES

Coordonnateur: Françoise Flieder

Centre de Recherches sur la Conservation
des Documents Graphiques
36 Rue Geoffroy-Saint-Hilaire
75005 Paris
France

Lors de la dernière réunion de notre groupe de travail *Documents Graphiques et Enluminures*, qui s'est tenue à Zagreb en octobre 1978, un voeu avait été émis à l'unanimité des membres présents d'étendre l'activité de notre groupe aux problèmes concernant les matériaux photographiques.

C'est à Zagreb en effet que, pour la première fois, des collègues présentèrent des communications qui ont fait apparaître le besoin de se pencher, non plus exclusivement sur la conservation des matériaux traditionnels tels que papyrus, cuir, parchemin, papier, mais également sur la conservation des documents photographiques et cinématographiques.

Si ces matériaux posent des problèmes spécifiques, ils ont néanmoins beaucoup d'analogie avec les constituants des documents graphiques, c'est pourquoi nous avons pensé inclure dans notre groupe, du moins provisoirement, tous les travaux relatifs à la conservation et à la restauration des photographies.

Depuis une dizaine d'années, l'intérêt porté sur la préservation des documents graphiques et photographiques s'est très rapidement accru. On a vu se créer dans toutes les parties du monde des instituts de recherche ainsi que de nombreux ateliers de restauration. Des organismes nationaux et internationaux se sont développés, la plupart d'entre eux ayant leur propre publication et organisant des rencontres annuelles sur des thèmes variés.

Ne pouvant dresser une liste exhaustive de toutes les manifestations qui se sont déroulées à travers le monde depuis 1978, nous ne citerons ici que celles qui nous ont paru les plus importantes.

L'American Institute for Conservation of Historic and Artistic Works (A.I.C.) a organisé deux grandes conférences :

en 1979, à Toronto où, parmi les différents sujets traités, celui de la restauration des dessins et des peintures sur papier a fait l'objet de plusieurs exposés ;

en 1980, à San Francisco où la restauration des matériaux photographiques était une des principales préoccupations des participants.

En avril 1979, s'est tenu à Ottawa, sous les auspices du Canadian Conservation Institute (C.C.I.) un symposium sur la dégradation du papier et la conservation des matériaux photographiques.

En septembre 1979, l'Internationale Arbeitsgemeinschaft der Archiv-Bibliotheks- und Graphikrestauratoren (I.A.D.A.) a organisé, à Göttingen une rencontre internationale. Tous les problèmes de la restauration traditionnelle ont été évoqués : désinfection, neutralisation, asséchement, utilisation de matériaux synthétiques ; par contre, la restauration de masse n'a pas fait l'objet de communications particulières.

A la bibliothèque de l'Université de Brême, s'est tenu en mai 1979, un symposium sur la restauration des encres et des enluminures de manuscrits. Les méthodes de révélation chimique et physique des textes effacés ont été largement discutées. La fabrication des couleurs et leur comportement sur le papier et le parchemin ont été étudiés ainsi que la restauration des miniatures.

La Society of Archivists et l'Institute of Paper Conservation ont organisé à Cambridge, en octobre 1980, une conférence internationale sur *The Conservation of Library and Archive Materials and the Graphics Arts*. Différents sujets ont été abordés : formation de personnel, conservation et restauration des cuirs et parchemins, restauration des papiers (neutralisation, nettoyage et renforcement), techniques relatives au montage des dessins.

Enfin, l'Institut de Rochester, qui a créé en 1969 une nouvelle revue *Photographic Conservation*, a organisé deux séminaires par an sur des thèmes spécifiques relevant de la préservation et de la restauration des images.

Par ailleurs, de nombreux ouvrages ont paru ces deux dernières années particulièrement dans le domaine de la restauration des photographies anciennes et des papiers. Le nombre sans cesse croissant des documents à protéger, a orienté les récentes recherches sur la mise au point de traitements de masse, faisant appel à des procédés rapides, réversibles et fiables ; la désacidification ayant été l'une des préoccupations prioritaires, c'est la raison pour laquelle il ne nous a pas paru opportun de présenter cette année encore des publications à ce sujet. et préférons renvoyer les membres de notre groupe aux multiples communications faites à ce propos.

Des progrès considérables ont été réalisés tant pour le comblage des lacunes à l'aide de pulpe à papier que pour le renforcement des documents devenus cassants, par contre, les études menées sur la conservation du cuir et du parchemin sont moins nombreuses. Il semblerait donc nécessaire de porter nos efforts dans ce sens pour les années à venir, tout particulièrement en ce qui concerne la renourriture des cuirs, leur teinture ainsi que le nettoyage des parchemins.

Les vingt-deux communications que nous présentons au cours de cette réunion émanent de onze pays différents : Autriche, Canada, France, Hongrie, Inde, Italie, Pays-Bas, Royaume-Uni, Tchécoslovaquie, U.R.S.S., Yougoslavie.

Quatre thèmes seront abordés :

- analyse scientifique des matériaux et des mécanismes de leur détérioration ;
- mise au point de nouveaux procédés de restauration ;
- description de travaux de restauration ;
- matériaux photographiques.

APERCU SUR QUELQUES OUVRAGES PARUS DEPUIS 1978

- BAKER (John P.) and SOROKA (Marguerite C.), Ed., *Library conservation : preservation in perspective*, Stroudsburg, Dowden, Hutchinson & Ross, 1978, 459 p. (The Information Sciences)
- BARGER (Susan M.), *Bibliography of photographic processes in use before 1880 : their materials, processing and conservation*, Rochester, Graphic Arts Research Center, 1980, 149 p.
- CLAPP (Anne F.), *Curatorial care of works of art on paper*, 3rd ed., Oberlin, Intermuseum Conservation Association, 1978, 135 p.
- CRAWFORD (W.), *The keepers of light : a history and working guide to early photographic processes*, New-York, Morgan & Morgan, 1979
- EASTMAN KODAK, Rochester, *Preservation photographs*, Rochester, Eastman Kodak, 1979, 48 p. , Kodak publication n° F 30, Cat 1113281
- HOFIG (Willi), *Zeitungspapier und Mikrofilm : ihre Lebensdauer im Bibliothekarischen Betrieb : Literaturübersicht (Papier journal et microfilm : leur durée dans les bibliothèques : revue de la littérature)*, Berlin, Deutscher Bibliotheksverband, 1979, 258 p. (A F B - Materialien, 24)
- LONDON (B.) and WITKIN (L.), *The Photograph collector's guide*, Boston, New-York Graphic Society, 1979
- LOUDEN (L.), *Paper conservation and restoration*, Appleton, Institute of paper chemistry, 1978, 91 p. (Bibl. ser. n° 284)
- REMPEL (Siegfried), *Le soin des collections de photographies en noir et blanc*, Ottawa, Institut canadien de conservation, 1979-80 (Bulletin technique de l'I.C.C., 6 et 9)
- TROBAS (Karl), *Papierrestaurierung in Archiven, Bibliotheken und Sammlungen : probleme und methoden (Restauration du papier dans les ARchives, bibliothèques et collections privées)*, Graz, Akademische Druck und Verlagsanstalt, 1980, 307 p.



SOME ASPECTS CONCERNING DEGRADATION PHENOMENA
OF PAPER CAUSED BY GREEN COPPER CONTAINING
PIGMENTS

Gerhard Banik and Johann Ponahlo

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



SOME ASPECTS CONCERNING DEGRADATION PHENOMENA OF PAPER
CAUSED BY GREEN COPPER CONTAINING PIGMENTS

Gerhard Banik and Johann Ponahlo

Gerhard Banik
Institut für Farbenchemie
Akademie der Bildende Künste
Wien
Austria

Johann Ponahlo
Geotechnisches Institut der Bundesversuchs- und
Forschungsanstalt Arsenal
Wien
Austria

ABSTRACT

IR studies concerning degradative properties of some copper compounds with cellulose gave indications for combined influence of SO_2 and sunlight with wavelengths above 330-340 nm.

Different types of copper acetate showed no uniform behaviour but gave stronger effects than copper chloride, whereas malachite, schweinfurt green and calcium-copper acetate were proved to be inert, as far as the present research work could be carried out.

1. INTRODUCTION

Green copper-containing pigments were important colouring matters in the field of graphic arts, although the use in these pigments presented problems for the artist and later for the conservation. Changes in hue and in many cases the destruction of the paper or parchment carrier were observed. Some theories and alligations concerning this problem are mentioned in the literature, but no precise results of investigations are given. WEHLTE (1) points out the bad compatibility of verdigris with other colouring matters, KÜHN (2) supposes that copper-acetate (verdigris) is slowly splitting off acetic acid and that this reaction causes the degradation of paper. There are a number of proposals to stop this process of degradation by chemical methods. Among others addition of alkaline earth metal-ions as calcium and magnesium seems to be effective (WILLIAMS et al. 3). Chelating agents should exhibit similar properties. But the chemical mechanisms of these inhibitory reactions are not well understood so far.

Today's conservation treatment of these damaged objects is confined mostly to bleaching the brownish areas by means of H_2O_2 and patching the destructed parts of the paper carrier (WÄCHTER 4).

The reason for a study of the detrimental behaviour of different copper-containing pigments towards paper was motivated through restauration problems with a valuable book on historic costumes from 16 century (owned by Austrian National Library, Theatre Collection):

BRUYN, Abrahan de,: Imperii ac sacerdotii ornatus
Diversarum item gentium peculiaris
vestitus. Adiunxit commentariolos
Caesarum, Pontificum ac Sacerdotum
Hadrianus Damman, Coloniae 1578.

The object contained water-coloured engravings made with a great variety of green pigments. A number of these engravings was damaged showing various stages of the described destruction process. Original samples of the different stages of decomposition could be easily taken.

2. PREVIOUS RESULTS OF CHEMICAL INVESTIGATIONS

Recent investigations were made by x-ray diffraction, scanning electron microscopy (SEM) in connection with energy dispersive spectrometry (EDS), microchemical tests and IR-spectroscopy (5).

The following results were obtained:

- 1) Any structural identification of the green pigments occurring on deteriorated areas has shown to be extremely difficult due to heterogenous composition, x-ray amorphous character of these substances and lack of corresponding materials.
- 2) The few cases when identification was possible were malachite, basic copper chloride, the latter being similar to atacamite by its chemical composition, langite and verdigris. In all these cases the samples were taken from areas showing a good state of preservation.
- 3) There was no doubt about the presence of copper-(I)-compounds along with original copper-(II)-compounds in deteriorated areas.
- 4) By means of IR-spectroscopy it could be shown that cellulose and some copper pigments react spontaneously when brought into contact. Furthermore pigments and

cellulose in mixture yield spectra different from those of the isolated components. The conclusion drawn would be that the chemical mechanism will certainly include effects of decomposition of both, the cellulose and the green pigment.

These results gave strong evidence that the destruction could be caused by several different reaction mechanisms. The occurrence of copper-(I) implicates the existence of a reducing substrate, i.e. reducing carbohydrates (Fehling-type reaction), sulfur dioxide or carbon monoxide, the latter two being present only occasionally. The occurrence of reducing carbohydrates requires some primary reaction mechanisms leading to their formation from cellulose. It seems, therefore, to be necessary to discuss the possible forms of decay of cellulose leading to such reducing compounds. The influence of heavy metal-ions such as copper-(II), should play an important role in this process.

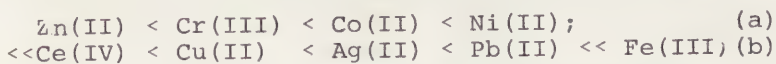
3. FURTHER IMPLICATIONS CONCERNING THE POSSIBLE DECOMPOSITION OF CELLULOSE CAUSED BY HEAVY METAL-IONS

It is well known to the paper industry that heavy metal-ions, such as Fe(III), Cr(III), Cu(II), Co(II), Mn(II), Zn(II), Ag(II), Pb(II) and Ce(IV) are acting as catalysts in the degradation of cellulose. Quite substantial work has been undertaken to elucidate the mechanisms of such processes (6). There is evidence that these transition metal-ions have to be considered as photosensitizers. In presence of these metal-ions only short exposure to light could instigate photochemical processes leading to radical formation as starting step for decomposition of cellulose.

Thorough investigations by HON (7-10) have led to the following conclusions:

1) Visible light with wavelengths above 330-340 nm occurring in closed rooms is able to induce radical processes, like the formation of alkoxy radicals, dehydroxylation and dehydrogenation of the cellulose molecule in presence of heavy metal-ions.

2) Heavy metal-ions can be classified into two groups according to their photosensitizing activities:



Fe(III) is the most active sensitizer followed by Pb(II), Ag(II) and Cu(II),

- 3) Humidity plays an important role in radical formation and accelerates the decomposition process of cellulose. Confirmatory results of WILLIAMS et al. (3) concerning the influence of copper-(II)-compounds on the folding endurance as an estimation for increase of brittleness in the course of aging in dry or humid atmosphere led to the conclusion that dry storage should minimize the effect of oxidative catalysts and oxidation.
- 4) Presence of lignin up to concentrations of 8% seems to have a retarding influence.
- 5) The reactions are considered to take place preferably within the amorphous part of the cellulose molecule.
- 6) Different kinds of cellulose fibres, such as linters, rayon, or amorphous cellulose react in different ways depending on their sorptive properties for heavy metal-ions.
- 7) Discolouration of cellulose in most cases takes place due to the formation of chromophoric groups like carbonyl and aldehyde groups or $>C=C<$ double bonds.

4. IRS-INVESTIGATIONS

4.1. Sample preparation

Difficulties to identify occurring compounds in original samples taken from destructed areas necessitated an explanation of the chemical mechanism of paper damage by means of simulation experiments. The results of which should provide suitable chemical methods for inhibition. IR-spectroscopy proved to be useful for tracing changes of chemical bonding and therefore was a valuable method to investigate the samples of simulation experiments. Copper compounds tested are summarized in table 1. The cellulose samples were taken from a 100 years old paper supplied by the Austrian Institute for Wood and Paper Research. Original samples could be taken in micro-amounts from the object mentioned above supplied by the Austrian National Library.

The cellulose samples were ground in an agate mortar and thoroughly mixed with the pigment (1:1). After treatment samples were pelletized with KBr according to the method of HURTUBISE and KRÄSSIG (11) (2 mg sample to 200 mg KBr). Spectra were obtained by means of a Perkin-Elmer IR-spectrometer 247 in the wavelength range between 4000 cm^{-1} and 650 cm^{-1} .

Table 1: COPPER COMPOUNDS USED FOR IRS-STUDIES

PIGMENT	FORMULA	ORIGIN	COLOUR	REMARKS
copper acetate (neutral verdigris)	$\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$	Merck No. 2710	blue green	IRS proved x-ray proved
"French verdigris"	heterogenous sample	+)	blue to bluegreen	according to IRS probably a mixture of neutral and basic copper- acetate, contains alkaline earth acetate
verdigris (I) (gemeiner)	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	+)	bluegreen	IRS proved x-ray-proved
schweinfurt green	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 3\text{Cu}(\text{AsO}_2)_2$	+)	bright green	IRS proved x-ray proved
copper chloride	$\text{CuCl}_2 \cdot x\text{H}_2\text{O}$	Merck No. 2732	light green	IRS proved
malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$	mineral sample, Zaire	green	IRS proved
basic verdigris (II)	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{Cu}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$	synthetized (12)	blue	IRS proved x-ray prove
basic verdigris (IV)	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot [\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$	synthetized (12)	dark green	IRS proved x-ray proved
calcium-copper acetate	$\text{CaCu}(\text{CH}_3\text{COO})_4 \cdot 6\text{H}_2\text{O}$	synthetized (13)	blue	IRS proved x-ray proved
+) pigment collection of the Institute of Colour Chemistry, Academy of Fine Arts, Vienna samples dated from late 19th century, origin and manufacture unknown				

4.2. Results

To study oxidizing properties it was necessary to investigate cellulose-pigment mixtures after drying at 60° and accelerated aging at 165° in dry atmosphere in unpelletized state. The results of these tests are summarized in table 2. From these results two important conclusions could be drawn:

- 1) Evidence for chemisorption of all different types of copper acetate on cellulose is given by reduction and disappearance of the acetate bands in IRS below 1100 or 700 cm^{-1} . This process takes place at room temperature upon contact of the components. Chemisorption was connected with changes in hue.
- 2) Oxidation bands of cellulose occurred with all copper compounds tested except schweinfurt green. Oxidation of cellulose normally proved by bands of carbonyl or $>\text{C}=\text{C}<$ double bonds at 1735-1700 cm^{-1} could not be detected in IRS of original degraded samples. Obviously the natural aging and decomposition process does follow other chemical mechanisms than oxidation reactions.

Another destructive influence could be sulfur dioxide evolved through gas-lightning of libraries in the late 19th century. Similar effects might result from today's environmental conditions. Reducing reactions of copper-(II)-compounds, especially copper acetates, had been mentioned by MAIRINGER et al. (14). Simulation experiments were made by treating the unoxidized cellulose-pigment mixtures mentioned in table 2 with sulfur dioxide at room temperature. These investigations brought about the following facts:

- 1) With all pigment samples tested, exposure to SO_2 resulted in an immediate change in hue from green or blue up to yellow or brown.
- 2) Visual inspection and tests of mechanical properties of the samples showed a distinct drop or loss of strength.
- 3) Formation of copper-(I)-sulfites from all types of copper-(II)-acetates, expected according to the literature (15), could be confirmed by x-ray diffraction, IR-spectroscopy and microchemical tests by means of 2,2'-biquinolyl. Furthermore traces of metallic copper could be detected.

Table 2: OXIDATION TESTS OF CELLULOSE PIGMENT MIXTURES AND OCCURRENCE OF CHEMISORPTION PHENOMENA

SAMPLE PIGMENT/CELLULOSE (1:1)	COLOUR 60°	165°	OXIDATION 60° 165°	REMARKS CONCERNING IRS OF UNTREATED SAMPLES
copper acetate	turquoise blue	brown	--	strong reduction of bands of copper acetate below 700 cm^{-1}
"French verdigris"	turquoise blue	dark brown	--	very strong reduction of bands of copper acetate below 700 cm^{-1}
verdigris (I) (gemeiner)	turquoise blue	brown	--	distinct oxidation band 1735-1700 cm^{-1} distinct oxidation band 1730 cm^{-1} significant bands of acetate and (-OH) between 1100-650 cm^{-1} are missing
schweinfurt green	pastel turquoise	yellow	--	no significant change of bands of both compounds
copper chloride	yellow	brown	--	no significant change of bands
malachite	dark green	brown	--	no change in IRS of both compounds
basic copper acetate (II)	blue	dark brown	--	significant bands of acetate and (-OH) between 1100-650 cm^{-1} are missing
basic copper acetate (IV)	green	dark	--	some bands of acetate below 1100 cm^{-1} are missing, (-OH)-bands not changed

Table 2 continued

SAMPLE PIGMENT/CELLULOSE(1:1)	COLOUR		OXIDATION		REMARKS CONCERNING IRS OF UNTREATED SAMPLES
	60°	165°	60°	165°	
pure paper	white	yellowed	--		weak oxidation band 1720 cm ⁻¹

- 4) Among the copper compounds tested, copper-(II)-chloride was the most susceptible to chemical changes in the course of SO_2 treatment.
- 5) There was strong evidence that chemisorptive bonding between cellulose and the different types of copper acetate was nullified by SO_2 .
- 6) Evaluation of IR-spectra showed no chemical similarity between degraded original samples and samples artificially aged by SO_2 or by combined treatment with SO_2 and accelerated aging at 165° .

According to these results the influence of SO_2 cannot be the main reason for the degradation process observed in original samples. But these tests gave valuable hints as to the chemical stability of cellulose-pigment mixtures.

The incompatibilities of the practical results with others presented in the literature led to the assumption that daylight might play an important role in these degradation processes. To simulate the conditions prevailing in a library under daylight conditions a quartz lamp equipped with a filter (pyrex glass, 2 mm, + acrylic glass, 7 mm) excluding radiation below 330 - 340 nm under temperature control ($<50^\circ$) was used. Previous tests proved the absence of any change in IRS if temperature was kept below 60° . It, therefore, could be concluded that any further change noticed during the irradiation tests was due to the irradiation itself. The results of these tests can be looked up in table 3.

From the data of table 3 one can follow that there is enough evidence that light (wavelengths $>330\text{-}340\text{ nm}$) is capable of causing degradation effects on paper coated with copper compounds. With the used irradiation time of 75 hours three compounds, schweinfurt green, malachite and calcium-copper acetate proved to be inert, as far as IRS was concerned. While the others (different types of copper acetate and a copper chloride) showed changes of spectra indicating chemical alterations of the pigment absorbed on cellulose. From the IRS of the irradiated pure paper no significant influence of radiation could be deduced. Paper samples containing special copper compounds gave minor, not always uniform but very significant changes in the IRS of β -cellulose. To find an interpretation for these changes of bands further experiments are under way. Probably, these reactions induced by short-time-irradiation are the initial step of the degradation of the cellulose.

Table 3: RESULTS OF IRRADIATION TESTS OF CELLULOSE PIGMENT MIXTURES WITH ARTIFICIAL SUNLIGHT >330 - 340 nm

SAMPLE DRIED AT 60°	COLOUR		EFFECTS OF IRRADIATION IN IRS OF SAMPLES AFTER 75 HOURS IRRADIATION TIME
	UNTREATED	TREATED	
copper acetate	turquoise blue	greenish blue	slight reduction of intensities of bands of cellulose, re-appearance of low-frequency-bands of copper-acetate
"French verdigris"	light turquoise blue	green	reduction of bands of cellulose, some new bands in the low-frequency range
verdigris(I) (gemeiner)	turquoise	green	reduced intensities of bands of cellulose, changes of bands of copper acetate
schweinfurt green	pastel turquoise	very light yellowish green	no significant change of IRS
copper chloride	yellow	greenish yellow with brown tint	strong reduction of band intensities of cellulose, especially those indicative of amorphous cellulose, reduced bands of H ₂ O and (-OH)
malachite	green	light green	no significant change of IRS
basic copper acetate (II)	turquoise blue	turquoise	marked change of bands of acetate between 1400-1200 cm ⁻¹ and of (-OH) groups below 900 cm ⁻¹
basic copper acetate (IV)	green	light greyish green	strong reduction of bands of acetate and cellulose, new band (not assigned) at 1635 cm ⁻¹
Ca-Cu-acetate	blue	rich blue green	no significant change of IRS
pure paper	white	white	no significant change of IRS

presence of SO_2 distinctly accelerated such reactions induced by the irradiation. Furthermore combined treatment of samples with SO_2 and irradiation led to spectra similar to those produced with original samples taken from damaged areas.

Fig.1 and 2 show the observed changes in IRS of "French verdigris" and cellulose caused by the discussed treatments.

5. CONCLUSIONS

Accelerated aging of the cellulose-pigment mixtures by means of temperature treatment makes obvious that general oxidation processes (leading to carbonyl and/or >C=C< double bonds in the cellulose) is not responsible for damaging effects caused by natural aging.

It is evident that all types of copper acetate were chemisorbed on cellulose substrate.

The influence of dry and wet SO_2 -gas which is still under investigation produced IRS different from the IRS of naturally aged original samples. Temperature treatment afterwards did not lead to similar spectra, either. Therefore SO_2 is not considered to be the single and predominant factor for the discussed process.

In several cases light with wavelengths above 330-340 nm caused chemical changes of both components (copper compound and β -cellulose) at least after 75 hours irradiation time. These findings corroborate the results of experimental and theoretical investigations made by HON (7-10) concerning the influence of heavy metal-ions on the photosensitized degradation of cellulose. Combined treatment with SO_2 and irradiation (wavelengths above 330-340 nm) led to IR-spectra already similar to those of original samples. It should be noted that the copper compounds tested showed no uniform behaviour towards cellulose. It is of importance to mention the stability of some tested cellulose-pigment mixtures containing schweinfurt green or calcium-copper acetate against oxidation and irradiation treatment, as far as IRS is concerned. These substances could produce inhibitory effects.

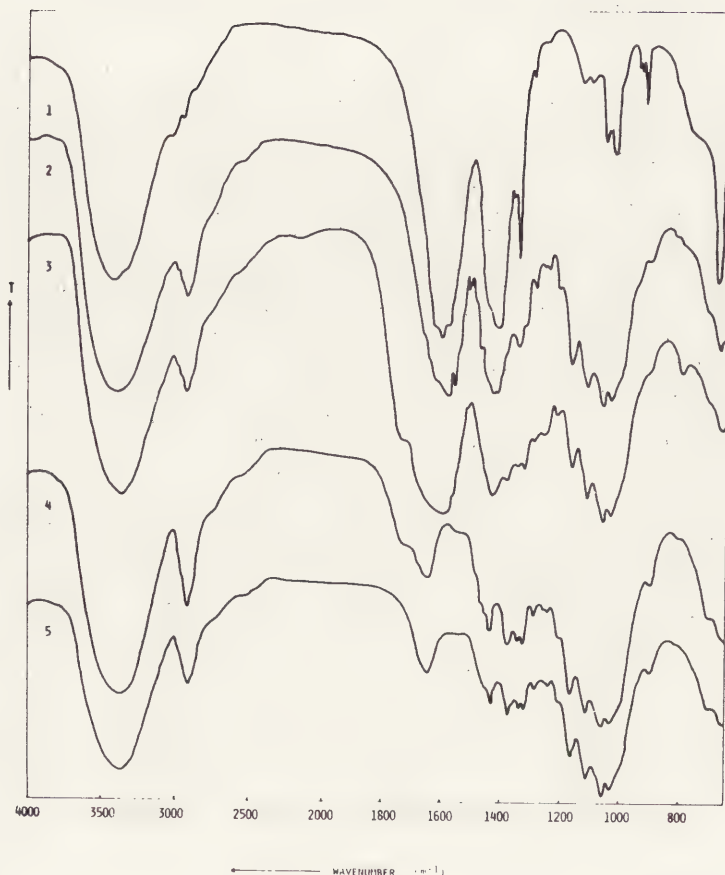


Fig.1: IRS spectra of samples and standard materials

1. "French verdigris" standard sample
2. Mixture of "French verdigris" and cellulose (1:1)
3. Mixture of "French verdigris" and cellulose treated at 165°
4. Standard cellulose sample treated at 165°
5. Standard cellulose sample untreated

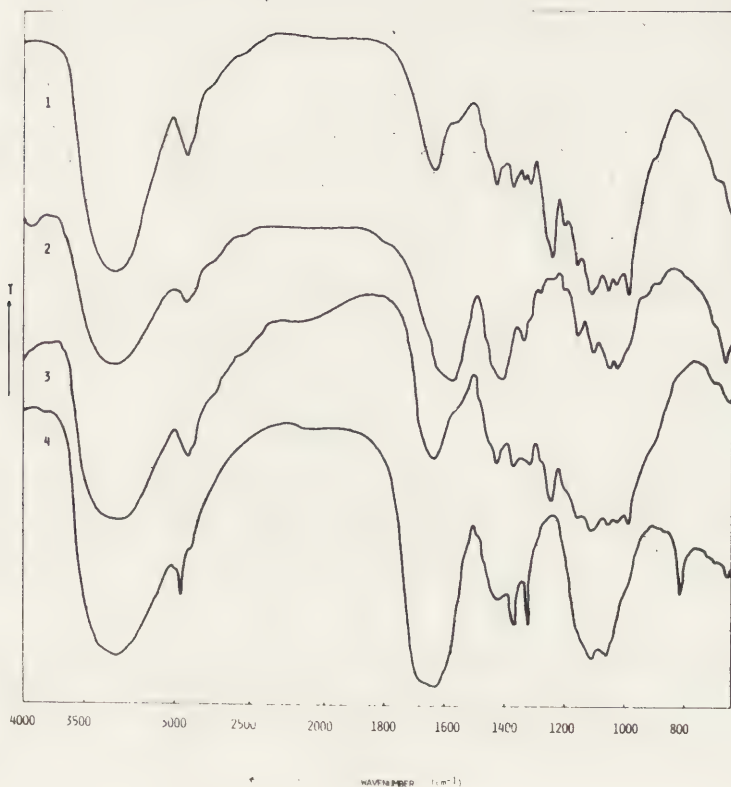


Fig.2: IRS spectra of samples and standard materials

1. Mixture of "French verdigris" and cellulose treated with SO_2
2. Mixture of "French verdigris" and cellulose exposed 75 hours to radiation (wavelengths $>330\text{-}340\text{ nm}$)
3. Mixture of "French verdigris" and cellulose treated with SO_2 and irradiation (irradiation-time 1 hour)
4. Original sample, paper carrier browned and embrittled, blue-green pigment, not identified

6. REFERENCES

1. Wehlte, K., Werkstoffe und Techniken in der Malerei, Ravensburg, 1967
2. Kühn, H., Die Erhaltung und Pflege von Kunstwerken, München, 1974
3. Williams, J.C., Fowler, C.S., Lyon M.S., Merrill, T.L., "Metallic Catalysts in the Oxidative Degradation of Paper", in: Preservation of Paper and Textiles of Historic and Artistic Value, Advances in Chemistry Series 164, Am.Chem.Soc., Washington, 1977
4. Wächter, O., "Die Konservierung von Globen und Landkarten", in: Kartensammlung und Kartendokumentation, No.4, Bad Godesberg, 1968, p.38
5. Banik, G., Stachelberger, H., Mairinger, F., Vendl, A., Ponahlo, J., "Investigations concerning the Problem of 'Kupferfraß' in Illuminated Manuscripts", Microchim. Acta, in the press
6. Egerton, G.S., "Photochemistry in Relation to Textiles" Proc. Symp. Harrogate, 22., 23.24.9.1949, pp 180 Soc.Dyers and Colorists, Bradford, Yorkshire, 1950
7. Hon, N., "Formation of Free Radicals in Photoirradiated Cellulose and Related Compounds", J.polym. Sci., polym. chem. Ed., 14, (1976) 2513 - 2525
8. Hon, N., "Formation of Free Radicals in Photoirradiated Cellulose, I. Effect of Wavelength", J.polym. Sci., polym. chem. Ed., 13, (1975) 1347-1361
9. Hon, N., "Formation of Free Radicals in Photoirradiated Cellulose, III. Effect of Photosensitizers", J.polym. Sci., polym. chem. Ed., 13, (1975) 1933-1941
10. Hon, N., "Formation of Free Radicals in Photoirradiated Cellulose, VIII. Mechanisms", J. polym. Sci., polym. chem. Ed., 14, (1976) 2497-2512
11. Hurtubise, F.G., Krässig, H., "Classification of Fine Structural Characteristics in Cellulose by Infrared Spectroscopy", Anal. Chem., 32, (1960), 2, 177-181
12. Schweizer, F., Mühlethaler, B., "Einige grüne und blaue Kupferpigmente", Farbe und Lack, 74, (1968), 12, 1159-75
13. Holden, A., Singer, P., "Crystals and Crystal Growing", New York, 1960, p. 115
14. Mairinger, F., Banik, G., Stachelberger, H., Vendl, A., Ponahlo, J., "The Destruction of Paper by Green Copper Pigments Demonstrated by a Sample of Chinese Wallpaper", Contribution to IIC-Congress, Vienna 1980
15. Ramberg, L., "Über die Kuprosulfite von Etard und Rogojski", Z. Phys. Chem., 69, (1910) 512-522

ACKNOWLEDGEMENT:

We are grateful to Prof.Dr.F.Mairinger making it possible to carry out this work. We owe Mrs.L.Fleck thanks for the careful routine IRS.

Authors are indebted to the Volkswagen foundation for financial support.

81/14/2

LA TECHNIQUE D'ECRITURE ET D'ENLUMINURES
DES MANUSCRITS ANCIENS SERBES

Vera Radosavljević

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Documents graphiques et
photographiques



LA TECHNIQUE D'ECRITURE ET D'ENLUMINURES DES MANUSCRITS ANCIENS SERBES

Vera Radosavljević

Narodna biblioteka Srbije
Skerlićeva 1
Beograd 11000
Yougoslavie

RESUME

Ce travail est poursuivi en vue de fournir une aide aux historiens d'art pour une meilleure connaissance de diverses techniques d'écriture et d'enluminure et aux restaurateurs et conservateurs pour mieux orienter leurs méthodes de traitement.

Une partie de ce rapport se propose de résumer les travaux réalisés dans l'identification des composants supposés avoir été utilisés dans la production des encres noires des manuscrits anciens, tandis que l'autre partie est exclusivement consacrée aux pigments et liants utilisés dans les couches picturales des enluminures des manuscrits serbes.

On a utilisé les différentes techniques d'identification: microscopie, analyses microchimiques, spectrophotométrie infra-rouge, colorations spécifiques sur coupes minces, chromatographie en phase gazeuse, microfluorescence X.

Les échantillons examinés font partie des manuscrits du XII^e jusqu'au XVIII^e siècle. Les résultats obtenus suggèrent la conclusion générale:

1. Dans la période qui s'étend du XII^e au XVII^e siècle, selon l'analyse de 35 échantillons, on a utilisé surtout les encres ferro-galliques, seulement deux étaient les encres mixtes, l'une au carbone, l'autre à l'indigo. Le liant était toujours la gomme, quoique selon les recettes la gélatine et la farine pouvaient être utilisées.

2. La plupart des pigments étaient les pigments minéraux (malachite, azurite, lapis-lazuli, orpiment, ocres), un certain nombre étaient les pigments organiques (indigo, laques ou extraits végétaux). On a utilisé l'or et l'argent et leurs substituts.

3. Les liants principaux étaient diverses gommages, blanc d'oeuf, gélatine. On pourrait dire que les manuscrits étaient écrits et peints dans la plupart des cas de la même manière que dans des autres pays d'Europe en ce temps là.

INTRODUCTION

Les recherches concernant les enluminures dans les manuscrits anciens qui dans l'art, surtout, dans l'art médiéval, ont un rôle important, étaient réduites aux études de style, des caractéristiques d'expression artistiques, c'est à dire aux études de leurs valeurs, des messages, des relations avec le texte, etc. La technique de cette peinture est devenue intéressante pour la science il y a peu près 20 ans notamment à cause des problèmes qui se posent pendant des travaux de conservation des enluminures et autres ornements des manuscrits endommagés dans la suite des siècles. La situation est pareille en cas des études de techniques d'écriture.

De bons résultats sont déjà obtenus au Centre de Recherches sur la Conservation des Documentes Graphiques à Paris, où on a introduit quelques méthodes de recherches sur les matières utilisées pour les enluminures ainsi que les encres (1).

Nombreux chercheurs hors du Centre ont déjà étudié la nature des liants et pigments dans la couche picturale des autres espèces de peintures, mais utilisés aussi par les enlumineurs. Au Laboratoire de Conservation de Bibliothèque nationale de Serbie on a étudié des nombreuses sources écrites sur les techniques utilisées par les enlumineurs, ainsi que des traités consacrés à l'art d'autres peintures qui contenaient les descriptions des procédés utilisés par les enlumineurs. Les résultats de cette étude nous avons présenté au Conférence de l'Institut International pour la Conservation des Objets d'Art et d'Histoire à Lisabonne 1972 (2).

Le travail présent est en effet le prolongement de cette étude et son but est de déterminer à l'aide des techniques d'analyses, déjà mises au point, des encres, des liants et des pigments, en un mot, la technique d'écriture et d'enluminure des manuscrits serbes. Ce rapport résume les premiers résultats, parce que faute de temps nous n'avons pu terminer toutes les analyses nécessaires, c'est à dire, il donne des résultats sans certains détails qui seront communiqués séparément.

HISTORIQUE

L'illumination dans les pays serbes englobe la période de sept siècles. Selon le style et les thèmes, les décorations picturales des manuscrits sont classées en trois périodes. La première qui dure de la deuxième moitié du XII^e siècle jusqu'à la deuxième moitié du XIII^e siècle, ensuite la deuxième période qui s'étend de la deuxième moitié du XIII^e siècle jusqu'à la deuxième moitié du XV^e siècle et la troisième qui dure jusqu'à la fin du XVII^e siècle, où le livre imprimé supprime complètement les manuscrits.

Les enluminures serbes ont été exécutées dans la plupart des cas dans les manuscrits. Il y en avait aussi sur les rouleaux, les chartes, les diplômes, qui sont conservés en très petit nombre. Le plus ancien manuscrit conservé date du XII^e siècle quoique l'art de lire et d'écrire commence au IX^e siècle. Les manuscrits étaient ornés d'un côté pour mieux comprendre le texte et en même temps pour les embellir. Les manuscrits dédiés à la cour et aux seigneurs étaient ornés luxueusement, tandis que les ornements dans les livres pour le peuple étaient modestes.

Le nombre de données concernant les techniques d'écriture et d'enluminure anciennes, dont nous disposons aujourd'hui est très limité. Les renseignements les plus anciens nous viennent du XVI^e siècle. Les recettes sont notées, généralement en passant, dans les livres écrits pour l'usage en anglais. Le traité d'art le plus ancien préservé (XVI^e siècle) écrit par un Serbe est connu sous le nom „Manuel de Nektari” (3). Il contient presque bien classées les recettes pour la préparation des pigments et des liants, utilisés sans doute au cours de siècles, car les changements étaient rarement admis par les normes ecclésiastiques. Le manuel, selon son auteur, est basé sur „les coutumes grecques et la peinture d'église et la peinture murale”.

Consacré en premier lieu aux peintres, le manuel peut aussi donner des renseignements sur la technique de peinture des manuscrits quand il s'agit des pigments et des liants. Il contient un grand nombre de recettes, par exemple, comment on fait du minium, la manière de faire des blancs de plomb, vert-de-gris, comment il faut broyer le cinabre et les autres couleurs, comment il faut pulvériser l'étain, comment il faut préparer l'or, le procédé de préparation du „potal” (le substitut de l'or), la règle pour écrire sur le papier avec les substituts de l'or, comment il faut dorer le papier, comment il faut préparer la gélatine, la production de liant de gomme-cerisier, comment on fait le „tempera” des liants mentionnés, même comment on fait l'encre pour les scribes.

On peut trouver aussi des renseignements sur les encres noires et colorées, outre le manuel de Nektari, dans les manuscrits serbes du XVI^e-XVII^e siècle notés et décrits par Ljubomir Stojanović dans Le catalogue des manuscrits et des livres imprimés anciens, La collection de l'Académie royale

serbe, Belgrade (4) et dans le Catalogue de Bibliothèque nationale à Belgrade (5). Un manuscrit (R 17) dans la collection de la bibliothèque de Patriarchie à Belgrade comprend des données précieuses pour étudier l'écriture et l'enluminure des manuscrits. Il y a des recueils divers composés plus tard, mais recouvrant des copies de recettes plus anciennes. Leurs recettes ou „typiques” (les règles) se rapportent à la préparation des encres noires pour écrire le texte, à la pulvérisation de l'or, à la préparation des couleurs bleus, rouges, jaunes et autres, au broiement des pigments etc. Un certain nombre englobe les recettes pour préparer les pigments organiques de différents espèces de bois rouge — bois de Campêche, bois de Brésil etc.

TRAVAIL EXPERIMENTAL

Dans notre recherche nous avons utilisé les échantillons des encres noires et brunes, de même que des pigments prélevés sur les manuscrits datant du XII^e jusqu'au XVII^e siècles appartenant aux collections de manuscrits des monastères: Dečani, Pečka Patrijaršija, Sveta Trojica, Krka, Musée de l'Eglise Orthodoxe serbe de Belgrade, Académie serbe des sciences et des arts et la Bibliothèque nationale de Serbie. Ces échantillons ont été prélevés sur les endroits plus ou moins endommagés, certains ont été prélevés sur les manuscrits qui ont subi la restauration (ce dont on a tenu compte lors de l'interprétation des résultats des analyses des liants et des encres). La recherche a englobé au total 245 échantillons d'encres et pigments prélevés sur un manuscrit du XII^e siècle, 3 manuscrits du XIII^e siècle, 19 du XIV^e, 26 du XV^e, 9 du XVI^e et 7 du XVII^e siècles. Les encres étaient plus ou moins brunes ou noires. Quant aux pigments, nous avons pris tous ceux qui ont servi pour l'ornementation des manuscrits mentionnés.

Nous avons identifié tous les échantillons des encres et des pigments inorganiques, alors que les analyses des pigments organiques ne sont pas encore terminées. Il n'a cependant pas été possible de prélever des échantillons d'un certain nombre de pigments indubitablement organiques pour ne pas endommager le support car il était seulement coloré.

C'est grâce à la coopération des collègues du Centre de Recherches sur la Conservation des Documents Graphiques à Paris et à la gentillesse de Madame F. Fliedner qui a rendu possible cette coopération que la plupart des analyses ont pu être effectuées. Je tiens à remercier particulièrement Madame Michèle Darbour qui préparait sa thèse d'ingénieur-docteur au Centre et Mademoiselle S. Bonnassies qui ont effectué toutes les analyses à l'aide de chromatographie en phase gazeuse.

Une bien plus petite partie de travail a été réalisée grâce à la très grande gentillesse des Messieurs Ch. Lahnier, A. Duval et A. Leclaire, chercheurs au Laboratoire de Recherche des Musées de France, Palais du Louvre, qui ont fait les analyses à l'aide de la microfluorescence de rayons X.

TECHNIQUES D'IDENTIFICATION DES ENCREs

Pour l'examen de l'encre nous avons adopté les méthodes suivantes:

a. Examen par loupe binoculaire à faible grossissement pour déterminer l'homogénéité de l'encre, la quantité du liant et pour voir s'il n'y a pas de fibres de papier ou autre chose dans l'échantillon.

b. La solubilité dans l'acide chlorhydrique pour voir si l'encre contient du carbone ou autres composants insolubles, c'est-à-dire s'il ne s'agit pas d'encre mixte. Ensuite, la solution a toujours été examinée sur le fer à l'aide du ferrocyanure de potassium ($K_4Fe(CN)_6$) car, de cette façon il a été possible d'identifier, en même temps, la présence du cuivre. Ce procédé s'imposait parce que dans la littérature on affirme souvent que les encres de tannin peuvent être des encres de fer, mais aussi des autres métaux, surtout du cuivre, car sous la dénomination „vitriol” on entendait autrefois un sulfate de fer ($FeSO_4$) ou un sulfate de cuivre ($CuSO_4$).

c. L'identification des substances tannantes et des liants glucidiques supposés avoir été utilisés dans la fabrication des encres, a été réalisée à l'aide de chromatographie en phase gazeuse.

TECHNIQUE D'IDENTIFICATION DES PIGMENTS

Plusieurs méthodes ont été utilisées:

a. Examens par loupe binoculaire, en tant qu'examens préliminaires pour grouper les échantillons par couleur, pour voir leur structure, la grandeur et la forme du grain, la pureté, la quantité de liant, et, s'il est possible de voir s'ils contiennent des pigments organiques ou inorganiques.

b. Pour un nombre d'échantillons, quand déjà il a été possible par observation à l'oeil nu et par loupe binoculaire, de supposer de quel pigment il s'agit, surtout dans le cas de pigments purs, non mixtes l'identification a été faite par examens microscopiques, c'est-à-dire sur la base de la couleur et de la forme des écailles, des cristaux (p. ex. malachite, azurite) mais accompagnés de test sur cuivre.

c. Pour l'identification des pigments inorganiques on a utilisé des microanalyses routinières dont on se sert dans les autres branches de la peinture, décrites par J. Plesters (6) et R. I. Kaganovič (7).

Le fait que les mélanges de pigments ont été souvent utilisés pour les enluminures, nous a amené à procéder pour tous les échantillons aux tests sur tous les cations dont la présence était possible de même que sur les anions là où ils pouvaient mieux définir le pigment. Nous avons toujours vérifié la présence du blanc de plomb à cause de l'habituelle dégradation des pigments avec ce blanc.

d. Lorsque les échantillons étaient tellement petits, que toutes les analyses nécessaires n'ont pas pu être faites, ou lorsqu'on pouvait douter si les résultats ainsi obtenus étaient valables ou non, on a utilisé la microfluorescence de rayon X.

e. L'identification des pigments organiques rouges a été effectuée pour le moment uniquement sur la base de changement de couleur lors de la dissolution dans l'ammoniaque, dans l'hydroxyde de sodium et dans l'acide sulfurique. Cependant comme cette méthode de travail donne des résultats douteux et que les examens faits par la spectrophotométrie infra-rouge ne nous ont pas donné de résultats visés, parfois à cause du volume de l'échantillon mais surtout à cause de sa pureté et la difficulté de séparer le pigment du liant, pour un certain nombre de couleurs, surtout celles employées pour les titres, l'identification a été faite par comparaison de l'original avec un catalogue de référence obtenu des échantillons des pigments faits selon les recettes anciennes. Pour l'indigo nous nous sommes servis de tests microchimiques selon J. Plesters. Les autres pigments organiques n'ont pas été analysés.

TECHNIQUE D'IDENTIFICATION DES LIANTS

a. Puisque la méthode des tests spécifiques utilisée au Laboratoire de Recherche des Musées de France pour l'identification de liants sur coupe mince, après l'étude théorique des méthodes de travail possibles, a paru très appropriée et facile à exécuter, il a été décidé d'examiner la possibilité d'appliquer cette méthode lors de la détermination du liant dans les enluminures. Nous nous en sommes tenus strictement aux instructions publiées pour la détermination des protéines avec le Noir Bleu Naphtol 10 B à différentes pH, sans chauffage (8).

b. Pour vérifier les résultats obtenus par la méthode de tests spécifiques, quand il était question de gomme, nous avons effectué dix analyses au moyen de la chromatographie gazeuse. Pour vérifier les résultats obtenus pour les liants qui, selon les tests spécifiques étaient des protéines, on a, en plus, effectué 6 analyses par la méthode de chromatographie sur couche mince d'après les instructions données par Madame De Pas (9). Les résultats qui, selon les tests spécifiques, donnaient la gélatine comme liant, ont été vérifiés par le test d'Erlach (10).

DISCUSSION DES RESULTATS ET DES METHODES DE TRAVAIL

Comme toutes les autres méthodes utilisées ont été déjà suffisamment commentées ailleurs, nous allons exposer ici seulement quelques observations sur la méthode des tests spécifiques de E. Martin, le test d'Erlach et la chromatographie en phase gazeuse (non pas en général mais uniquement

sous l'angle des résultats obtenus et du but de ce travail).

La méthode de colorations spécifiques sur coupe mince s'est montrée très pratique dans un certain nombre de cas; cependant, existent toutefois certaines réserves qui ne permettent pas de la considérer comme tout à fait valable dans tous les cas.

Lors de l'examen des couches colorées claires, l'identification ne pose pas de problèmes car l'intensité de la coloration au moyen de Noir Amide₁ et Noir Amide₃ est généralement facile à distinguer, mais pour les couches sombres et en particulier pour les couches bleues, surtout si elles ne sont pas riches en liant, l'identification est difficile car les différences dans l'intensité de la coloration ne sont pas faciles à discerner. L'identification devient difficile aussi quand le liant est complexe, p. ex. la gomme plus la gélatine ou la gomme plus le blanc d'oeuf car, dans la plupart des cas, la gomme ne reçoit pas la couleur et c'est en fait par là qu'elle est identifiée. Parfois, lorsque la gélatine seule ou le blanc d'oeuf seul sont des liants, la différence dans l'intensité de coloration avec le Noir Amide₁ et le Noir Amide₃ n'est pas perceptible. Dans ce cas on peut seulement constater qu'il s'agit des protéines.

Les analyses de contrôle effectuées au moyen de la chromatographie en phase gazeuse (dix échantillons choisis) ont montré que les conclusions qui se rapportent à la gomme comme liant, obtenues par la méthode de tests spécifiques étaient correctes, le contrôle pour 8 échantillons pour lesquels il n'était pas possible de déterminer par tests spécifiques, s'il s'agit du blanc d'oeuf ou de la gélatine, a montré dans 3 cas qu'il s'agit de la gélatine, alors que pour 5 échantillons on a pu seulement confirmer qu'il s'agit d'un liant protéinique. Ce contrôle a été effectué à l'aide de chromatographie sur couche mince. Pour trois échantillons pour lesquels il a été constaté au moyen de tests spécifiques qu'il s'agit de la gélatine, il a été confirmé, par le test d'Erlich que c'est bien de la gélatine dont il s'agit.

Quant au microtest d'Erlich, test spécifique pour la gélatine, on peut dire qu'il donne d'excellents résultats pour les quantités de gélatine entre 0,4 et 0,5 mg ce qui fait que l'on peut l'utiliser pour celle-ci dans les miniatures.

Un des buts du travail a été de déterminer l'origine des tannins utilisés dans la fabrication de l'encre. Pour cette raison on a fait des chromatogrammes (chromatographie en phase gazeuse) des extraits de noix de galle, écorce de chêne, frêne élevé et frêne fleuri, grenadier, aulne, fustel (sumac des teinturiers) qui, selon les traités anciens étaient le plus souvent utilisés comme sources de substances tannantes. On supposait que la comparaison de ces chromatogrammes avec les chromatogrammes des encres inconnues permettrait de déterminer les substances tannantes qu'elles contiennent. Bien que la séparation du sucre et des autres substances ait été par ces analyses excellente, le but n'a pas pu être atteint, en partie parce que les échantillons de l'encre examinés contenaient les gommes comme liants qui, par hydrolyse, pareillement aux tannins, donnent des sucres, ce qui empêchait de déterminer quelle est la partie qui provient du tannin et laquelle de la gomme. Les composants (c'est à dire les pics) sur la base desquels on pourrait éventuellement effectuer l'identification, ne se trouvaient pas dans les échantillons examinés. En outre, les chromatogrammes des extraits contenaient les pics non-identifiés et bien que leur identification ait pu peut-être donner la réponse, nous n'avons pas pu y procéder cette fois-ci faute de temps.

Les analyses de contrôle des résultats obtenus au moyen de colorations spécifiques sur coupe mince qui étaient effectuées à l'aide de la chromatographie en phase gazeuse ont montré que tous les liants examinés étaient des gommes. Il n'a pas pu être déterminé exactement de quelle espèce de gomme il s'agissait, mais le contenu de xylose et manose que la gomme arabique ne contient pas mais que par contre contiennent les gomme-pêcher, gomme-amandier, gomme-cerisier, gomme-griottier, gomme-prunier, permet de conclure qu'il s'agit de ces gommes-là, car selon les traités anciens elles étaient utilisées pareillement comme la gomme arabique.

Quant à l'identification des pigments organiques par comparaison aux échantillons connus, l'on peut dire maintenant que les laques et les extraits de bois de Brésil (et les autres bois rouges)

peuvent, en général, être identifiés avec certitude, surtout lorsque le manuscrit a des lettres (ce pigment est le plus souvent utilisé pour écrire les initiales et les titres) qui se sont jadis décolorées partiellement ou entièrement, ce qui permet de faire plusieurs comparaisons. La différence entre le kermès et la cochenille ne peut pas être déterminée de cette façon, mais on peut dire presque avec certitude qu'il s'agit de l'un ou de l'autre de ces pigments.

CONCLUSION

L'examen d'un grand nombre de manuscrits anciens serbes, l'étude de traités contenant des données sur les pigments, liants et technique d'enluminure, ainsi que les analyses effectuées jusqu'à maintenant, amènent à la conclusion suivante:

Les manuscrits cyrilliques serbes sont écrit avec des encres ferro-tanniques. Seulement 6 de 35 échantillons contenaient de l'acide gallique et l'on peut dire qu'elles sont ferro-galliques. Les autres sont composées soit des tannins végétaux ne contenant pas d'acide gallique, soit des tannins qui contiennent de l'acide gallique qui, dans le cours des temps, s'est décomposé pour différentes raisons et n'a pas pu être prouvé.

Deux des encres examinées étaient des encres mixtes. L'une contenait du carbone (XIV^e s.), l'autre de l'indigo (XIV^e s.), ce qui nous amène à la conclusion que les encres mixtes étaient moins utilisées et que celles au carbone ou bien n'étaient pas utilisées ou bien étaient utilisées dans un très petit nombre de cas.

Comme liant on a le plus souvent utilisé la gomme qui était ajoutée dans des proportions très variables et l'on composait les encres aussi des liants protéiniques et de la colle de farine, quelquefois pas bien tamisée.

Les analyses effectuées et les recettes anciennes montrent que les encres au sulfate de cuivre n'étaient pas produites.

Une grande partie de pigments utilisés étaient des pigments inorganiques, le cinabre (vermillon), minium, ocre, malachite, terre verte, azurite, lapis-lazuli (outremer), orpiment, céruse. Le vert-de-gris était identifié seulement trois fois, mais à juger selon les dégâts qui, sur de nombreux manuscrits, ont été provoqués par la couleur verte, là où aujourd'hui on peut identifier le carbonate de cuivre, le vert-de-gris était souvent utilisé. On a utilisé aussi l'or et l'argent ainsi que leurs substituts (étain, mercure, cuivre ou matières organiques).

Parmi les pigments organiques on a beaucoup utilisé, pour les lettres rouges, à partir du XIV^e siècle et plus tard, la laque de différentes espèces de la famille Caesalpiniaceae, préparée de diverses façons. Parmi les autres pigments organiques on a jusqu'à maintenant identifié l'indigo et le safran, à partir de XIII^e siècle. Sur la base de la couleur de certains pigments pour lesquels on peut affirmer qu'ils sont d'origine organique, on suppose que ce sont des laques des extraits d'une sorte de *Rhamnus*.

L'or a été utilisé sous forme de poudre et de feuilles, mais aussi on a utilisé souvent ses substituts d'origine organique ou inorganique.

Les liants étaient préparés soit à partir des sucres d'essences diverses (gomme arabique, gomme-cerisier, gomme-pêcher, gomme-amandier, gomme-prunier, gomme-griottier) soit à partir de colle de peau ou d'autres sortes de gélatine ou le blanc d'oeuf.

Les miniatures ou autres ornements ont été faits quelquefois directement sur le support et quelquefois on faisait des assiettes. Il y a des exemples où un même manuscrit faisait voir deux manières mentionnées de procéder.

D'après les miniatures et initiales non-terminées on peut dire que les enlumineurs serbes s'en tenaient quelquefois à l'ordre qui était de règle et quelquefois non. C'est-à-dire la règle demandait de faire d'abord les contours et puis de peindre en or, ensuite d'appliquer une seule couleur dans le manuscrit entier. Il y a beaucoup de manuscrits où l'on ne s'en tenait pas à ceci. Un même manuscrit

contient seulement des contours pour certaines initiales, drapeaux ou miniatures, alors que les autres sont partiellement ou complètement terminés. Il y a aussi des manuscrits dans lesquels les contours sont tracés et où l'or est enduit sur tous les ornements ce qui prouve que l'enlumineur respectait les règles.

REFERENCES

- (1) FLIEDER (F.). — Mise au point des techniques d'identification des pigments et des liants inclus dans la couche picturale des enluminures des manuscrits, *Studies in Conservation*, 13 (1968), pp. 49–86

- FLIEDER (F.), BARROSO (R.), ORUEZABAL (C.). — Analyse des tannins hydrolysables susceptibles d'entrer dans la composition des encres ferro-galliques, ICOM, Venise 1975, 15/12

- (2) RADOSAVLJEVIĆ (V.). — The Technique of Old Writings and Miniatures, *Conservation and Restoration of Pictorial Art*, Butterworths, London–Boston, 1976, pp. 202–206

- (3) PETROV (N. A.). — Les règles sur la peinture ecclésiastique et murale de l'évêque Nectari de la ville serbe Veles datant de 1599 et son importance pour l'histoire et la peinture russe, *Les écrits de SAI*, XI (1–2), Peterbourg

- (4) STOJANOVIĆ (Lj.). — Le catalogue des manuscrits et des livres imprimés anciens, La collection de l'Académie royale serbe, Belgrade, 1901, pp. 182 et 190

- (5) STOJANOVIĆ (Lj.). — Le catalogue de Bibliothèque nationale, vol. 4, pp. 377–378

- (6) PLESTERS (J.). — Cross-Sections and Chemical Analysis of Paint Samples, *Studies in Conservation*, 2(1956), pp. 110–157

- (7) KAGANOVIČ (R. I.). — Les méthodes d'analyse des pigments dans la peinture, *Communications*, Moskva, 1965, 14. pp. 34–68

- (8) MARTIN (E.). — Contribution à l'Analyse des Liants Mixtes, ICOM, Zagreb 1978, 20/8

- (9) DE PAS (M.). — Etat des travaux effectués sur l'analyse des constituants des encres noires par deux techniques: chromatographie sur couche mince et électrophorèse, ICOM, Venise 1975, 15/9

- (10) BROWNING (B. L.). — *Analysis of Paper*, Second edition, Marcel Dekker, INC, New-York and Basel, 1977, p. 102

LES ENCREs METALLOGALLIQUES: ETUDE DE LA
DEGRADATION DE L'ACIDE GALLIQUE ET ANALYSE
DU COMPLEXE FERROGALLIQUE

Michèle Darbour, Sylvette Bonnassies et
Françoise Flieder

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Documents graphiques et
photographiques

LES ENCREs METALLOGALLIQUES: ETUDE DE LA DEGRADATION DE L'ACIDE GALLIQUE ET ANALYSE DU COMPLEXE FERROGALLIQUE

Michèle Darbour, Sylvette Bonnassies et Françoise Flieder

Centre de Recherches sur la Conservation des Documents
Graphiques
36 rue Geoffroy-Saint-Hilaire
75005 Paris
France

Résumé

Nous avons étudié les causes et la cinétique de la dégradation de l'acide gallique dans les encres anciennes. Plusieurs facteurs ont été analysés, tant biologiques (influence de microorganismes) que physico-chimiques (chaleur sèche, chaleur humide, rayonnement). Les cinétiques ont été suivies par chromatographie en phase vapeur avec des colonnes capillaires de verre fabriquées au laboratoire. Les résultats ont montré que l'acide gallique est très sensible aux différents facteurs étudiés et principalement aux microorganismes et à l'humidité. Cependant, il n'apparaît aucun lien entre la disparition de l'acide gallique et le pâlissement des encres.

Pour essayer de comprendre ce dernier phénomène, nous avons entrepris de déterminer l'état du fer dans le complexe ferrogallique et dans les encres. Différentes techniques ont été expérimentées, dont l'effet Mössbauer qui nous a permis d'obtenir des résultats très prometteurs (analyse d'une encre d'un manuscrit du XVe siècle).

INTRODUCTION

Les recherches présentées ici font suite à différents travaux concernant l'étude des encres anciennes.

Mme DE PAS (5-6) s'est principalement intéressée aux techniques de fabrication des encres. En ce qui concerne les encres métallogalliques (seule classe que nous retiendrons pour cette étude), leur mise en oeuvre n'a pas évolué au cours des siècles. Il semble donc peu probable d'obtenir des renseignements sur la datation des manuscrits par la seule analyse des encres.

M. ORUEZABAL a étudié à l'aide de la chromatographie en phase vapeur (CPV) les différentes matières premières entrant dans la

fabrication des encres métallogalliques (9) ainsi que les constituants des encres prélevées sur des manuscrits du XI^e au XVI^e siècle (1). Les différences mises en évidence par ces analyses dans la structure chimique des substances tannantes ne sont pas suffisantes pour permettre leur identification. On ne peut donc pas, pour le moment, apporter des renseignements sur l'origine géographique des documents.

Cependant, deux points importants se sont dégagés de ces travaux. D'une part, les encres prélevées sur les manuscrits ne contiennent que très rarement de l'acide gallique et en très faible quantité : c'est pourtant le produit majoritaire de l'encre et c'est la formation d'un "complexe" entre celui-ci et le fer qui donne la couleur noire. D'autre part, les encres analysées sont presque toutes très noires, même si elles n'ont aucune trace d'acide gallique. Or, les expériences que Mme TALBOT a menées (23) ont montré qu'une des meilleures techniques de révélation des encres pâlies consiste à tremper le document dans une solution d'acide gallique. Nous sommes donc devant une ambiguïté : de nombreuses encres métallogalliques ne contiennent plus du tout d'acide gallique et sont pourtant restées très noires, alors que l'acide gallique régénère des encres pâlies. C'est pourquoi nos recherches se sont orientées sur la dégradation de l'acide gallique.

Dans la première phase de notre travail, nous avons perfectionné les méthodes d'analyses utilisées au laboratoire. Ceci nous a permis d'améliorer la séparation des différents constituants de l'encre et de diminuer la quantité d'échantillon nécessaire.

Nous avons ensuite étudié la dégradation de l'acide gallique par différents facteurs :

- les Anciens ayant coutume de laisser reposer l'encre avant de l'utiliser, nous avons examiné l'influence de différents cryptogames sur l'acide gallique de l'encre et sur ses autres constituants.

- Les manuscrits n'ayant pas toujours été conservés dans de bonnes conditions, nous avons également envisagé l'effet de différents facteurs climatiques sur cette dégradation.

Enfin, nous avons complété nos recherches par l'étude du complexe ferrogallique. Il nous a notamment paru intéressant de déterminer l'état du fer dans le complexe et dans les encres.

TECHNIQUES D'ANALYSE DES ENCREs

La chromatographie en phase vapeur a été perfectionnée par la mise en oeuvre au laboratoire des colonnes capillaires (4). Leurs caractéristiques sont les suivantes :

- verre Pyrex, traité par l'acide chlorhydrique et silylé (13) ;
- diamètre intérieur 0,2 à 0,3 mm, longueur 20 m ;
- phase stationnaire OV 1 (ou SE 52) déposée par méthode statique (solution à 0,2 %) (12).

Les analyses sont effectuées sur un appareil Girdel Série 3000, avec les conditions ci-dessous :

- gaz vecteur : azote
- injecteur et détecteur à ionisation de flamme à 280°C
- programmation de température de 120°C à 250°C à 3°C/minute
- défilement du papier 5 mm/minute
- atténuation 32, gamme 10⁻¹¹A pour 1 mV
- volume de l'injection 2 μ l

Avant d'être analysés en CPV, les échantillons font l'objet de deux traitements (9) :

- une hydrolyse qui permet de rompre les liaisons entre les différents constituants (pour 0,3 mg de produit, 1 ml d'acide chlorhydrique à 3 %, 4 heures à 105°C)
- une silylation, qui permet l'analyse des sucres et des acides phénoliques en CPV : l'hydrolysate est évaporé à sec, puis repris dans 30 μ l de pyridine. On ajoute 10 μ l d'hexaméthylidisilazane et 5 μ l de triméthylchlorosilane.

Ces techniques nous ont permis d'analyser l'encre de nombreux manuscrits d'époque et de provenance diverses. Nous ne présenterons ici que le chromatogramme de l'encre du missel de Colmar (fig. 1) : nous y retrouvons l'arabinose (pic noté 5), le galactose (pics notés 6), le glucose (pics notés 2) et l'acide gallique qui est en quantité importante pour une encre prélevée sur un manuscrit ancien (pic noté 1).

Bien que l'emploi des colonnes capillaires nous ait donné la possibilité d'analyser de manière beaucoup plus fine les constituants des encres, l'identification de la substance tannante utilisée n'est pas encore possible.

ETUDE DE LA DEGRADATION DE L'ACIDE GALLIQUE

Une étude bibliographique nous a permis de mettre en évidence de nombreuses références concernant la dégradation de l'acide gallique par les microorganismes.

JACOB et PIGNAL (14) ont montré que certaines souches de levures provoquent la décarboxylation de l'acide gallique.

Plusieurs équipes ont étudié l'action des bactéries sur cet acide ou sur des substances voisines (2-21-22). Les mécanismes proposés sont très proches : les premières transformations sont dues à l'oxydation de deux fonctions phénol en ortho (passage par une forme orthoquinone), puis à la rupture du cycle entre ces deux fonctions. Un des produits intermédiaires le plus cité est l'acide α -cétoglutarique.

FRIEDRICH (10), LEWIS et STARKEY (16), ainsi que DAGLEY (3) ont examiné l'influence des champignons (*Aspergillus*, *Penicillium*) sur

les tannins et sur l'acide gallique. Les résultats sont analogues à ceux obtenus avec les bactéries.

Par contre, nous n'avons relevé que très peu de références concernant la dégradation de l'acide gallique par des facteurs physiques. STAHL et KARIG (20) mentionnent la décarboxylation de cet acide par la chaleur. Quant à WEIGL (25), il s'intéresse à l'influence de la température et du taux d'hygrométrie sur la conservation des documents en général.

1. Dégradation biologique

Nous avons étudié l'action de l'*Aspergillus niger* sur l'acide gallique contenu dans les différentes solutions aqueuses suivantes :

- acide gallique à 1 %
- substances tannantes à 3 % (noix de galle, divi-divi)
- encres fabriquées selon une recette ancienne avec
 - 3 g. de sulfate ferreux
 - 3 g. de noix de galle
 - 3 g. de gomme arabique
 - 100 ml d'eau

Les différentes solutions sont stérilisées, puisensemencées avec des spores de champignons et placées dans une étuve bactériologique à 24°C. On effectue des prélèvements régulièrement afin de suivre la cinétique de dégradation de l'acide gallique. Ces analyses sont effectuées qualitativement en spectroscopie infra-rouge (IR) dans le cas de la solution d'acide gallique pur et quantitativement en CPV dans tous les autres cas. Tous les essais ont été menés simultanément avec et sans addition de 0,2 % d'un milieu nutritif formé de sels minéraux, qui favorise la croissance du champignon. Les résultats ont montré que ce milieu nutritif n'agit que sur la vitesse de dégradation et pas sur son mécanisme. De plus, les expériences étant menées sur plusieurs solutions, les cinétiques peuvent varier de l'une à l'autre.

Résultats

- Les analyses en IR ont mis en évidence trois étapes dans la dégradation par l'*Aspergillus niger* de l'acide gallique pur : un jour 5 jours, 8 jours, puis après 30 jours il ne reste plus de trace de l'acide gallique.

Malheureusement, si le spectre IR de l'acide gallique témoin est assez connu (24), il est difficile d'interpréter les spectres correspondant aux différentes étapes de dégradation car nous sommes en présence d'un mélange de plusieurs produits de détérioration. Il est à noter que le spectre IR de la première étape n'est pas en opposition avec la présence d'une forme orthoquinone dérivée de l'acide gallique.

Les analyses en CPV nous ont montré la disparition pratiquement totale de l'acide gallique contenu dans la noix de galle (ou le divi-divi). Les résultats les plus significatifs, correspondant à la dégradation de l'acide gallique par l'*Aspergillus niger* sont rassemblés ci-dessous :

	50 % de diminution	95 % de diminution
Avec milieu nutritif	5 à 10 jours	15 à 30 jours
Sans milieu nutritif	20 à 30 jours	90 à 120 jours

La figure 2 représente le chromatogramme de la noix de galle témoin dont les différents constituants sont : l'arabinose (pic 5), le rhamnose (pic 10), le fucose (pic 11), le xylose (pic 13), le mannose (pic 12), le galactose (pics 6), le glucose (pics 2) et l'acide gallique (pic 1). La figure 3 est le chromatogramme de la noix de galle dégradée par l'*Aspergillus niger* pendant 21 jours (avec milieu nutritif). Les principales différences sont la diminution très nette de l'acide gallique et l'augmentation sensible des pics notés A et B (ces pics rediminuent si on poursuit l'attaque). Des analyses en GCMS (spectrométrie de masse couplée à la CPV) ont déterminé la structure des produits correspondants : le xylose pour A et un pentose pour le pic B. Ces produits sont vraisemblablement dus au métabolisme de l'*Aspergillus niger*.

- La dégradation par l'*Aspergillus niger* de l'acide gallique dans les encres est beaucoup plus lente. Les figures 4 et 5 représentent les cinétiques de cette disparition : les solutions notées h, i, j, k, l, m sont des encres fabriquées de manière analogue mais seules les encres h, i, j (fig. 4) contiennent du milieu nutritif. Ces figures nous montrent que la disparition de l'acide gallique n'est totale qu'en présence de milieu nutritif.

Les analyses en CPV ont également mis en évidence l'apparition d'un nouveau produit lors de la dégradation de l'acide gallique dans les encres : sur le chromatogramme il se situe entre le galactose et le glucose, sa structure n'est pas déterminée.

- D'autres essais concernant les ellagitannins ont montré que l'acide ellagique résiste aux attaques microbiennes.

Nous avons montré que l'acide gallique se dégrade sous l'influence des champignons, qu'il soit pur, contenu dans une substance tannante ou dans une encre. Néanmoins, dans ce dernier cas, la dégradation n'est pas totale : il semble donc que le fer présent dans l'encre ait un effet inhibiteur.

2. Dégradation par les facteurs physiques

Nous avons suivi en CPV la dégradation de l'acide gallique d'une encre (même recette que p.4) soumise à différents facteurs tels que la chaleur humide, la chaleur sèche, le rayonnement. Dans tous les essais, nous avons retrouvé le produit apparu lors de la dégradation biologique de l'encre.

- L'influence d'une chaleur humide est très importante. La figure 6 représente les cinétiques de dégradation de l'acide gallique dans des encres soumises à 90 % d'humidité relative (H.R.) et aux températures de 60°C, 48,5°C, 35°C et 23°C : elles nous montrent la rapidité de la dégradation puisque, par exemple, 50 % de l'acide gallique disparaît en 10 jours à 60°C et 90 % H.R. et en 30 jours à 35°C et 90 % H.R.

- Les cinétiques de dégradation de l'acide gallique dans une encre soumise à l'influence de la chaleur sèche sont au départ très proches de celles obtenues sous chaleur humide (50 % de disparition en 12 jours à 60°C et en 30 jours à 35°C). Mais la dégradation ne se poursuit pas totalement : même à 60°C, on n'obtient que 85 % de disparition de l'acide gallique.

- Le rayonnement (lampe au xénon à 35°C et 85 % H.R. et lampe à vapeur de mercure à 35°C) n'a pas d'effet sur la dégradation de l'acide gallique contenu dans les encres (les cinétiques obtenues sont celles des chaleurs sèche et humide correspondantes). De plus, des analyses densitométriques ont montré que l'encre ne se décolore pas.

De toutes ces études, il ressort que l'acide gallique est très sensible à la chaleur et principalement lorsqu'elle est accompagnée d'humidité.

3. Dégradation mixte

Pour terminer cette étude de la dégradation de l'acide gallique, nous avons fait moisir une encre pendant deux semaines. Nous l'avons ensuite évaporée et soumise à différentes chaleurs sèches et chaleurs humides.

La cinétique de dégradation de l'acide gallique est plus rapide que dans le cas de la dégradation physico-chimique seule. Nous ne mentionnerons qu'un résultat très significatif : dans une encre moisie laissée à 23°C et 50 % d'humidité relative, 65 % de l'acide gallique se dégrade en 4 mois. La dégradation est ensuite très lente.

4. Conclusions

L'acide gallique se dégrade facilement sous l'influence de divers facteurs tant biologiques que physico-chimiques.

Lors de cette dégradation, nous n'avons pas mis en évidence l'acide α -cétoglutarique cité dans la littérature, mais un autre produit de structure indéterminé (nous n'avons pas pu effectuer d'analyse en GCMS). Notons qu'un pic ayant les mêmes caractéristiques chromatographiques est présent dans plusieurs analyses d'encre de manuscrit.

Les cinétiques de dégradation physico-chimiques de l'acide gallique sont telles que l'absence de cet acide dans une encre ancienne ne prouve pas que celle-ci ait subi l'action des microorganismes lors de sa fabrication. Par contre, si une encre ancienne possède

encore de l'acide gallique, nous pouvons penser qu'elle n'a pas été mois pendant sa fabrication.

ETUDE DU FER DANS LE COMPLEXE FERROGALLIQUE ET DANS LES ENCRE

Nous avons trouvé très peu de références concernant l'étude du complexe ferrogallique (7,17), mais des articles sur les complexes organo-métalliques nous ont permis de déterminer les méthodes d'analyse utilisables : titrimétrie et spectrophotométrie (18,19), spectroscopie électronique (15), effet Mössbauer, utilisé dans le domaine des peintures et poteries (8).

1. Titrimétrie-Spectrométrie-Spectroscopie électronique

Les analyses par titrimétrie et spectrométrie de différents mélanges de solutions d'acide gallique et de sulfate de fer (ferreux ou ferrique) ont montré la formation de complexe entre un atome de fer et deux ou trois molécules d'acide gallique mais uniquement dans le milieu alcalin. De plus, des essais en polarographie débouchent sur l'existence d'un équilibre du type quinone-hydroquinone pour l'acide gallique, dont l'étude approfondie nous entraînerait loin des encres anciennes.

Les analyses par l'ESCA (Electronic Spectroscopy for Chemical Analysis) n'ont pas fourni les résultats espérés car l'interprétation s'est avérée imprécise par absence d'un calculateur.

Les résultats les plus intéressants ont été obtenus par effet Mössbauer.

2. Effet Mössbauer

Les analyses ont été effectuées au Laboratoire de Spectrométrie Mössbauer du Centre d'Etudes Nucléaires de Saclay par M. IMBERT et son équipe.

Cette technique, basée sur l'absorption résonnante de rayonnement gamma entre une source et l'échantillon, permet d'étudier l'isotope 57 du fer. La source se déplace constamment autour d'une position d'équilibre afin d'obtenir un balayage en énergie par effet Doppler. A partir du spectre Mössbauer qui représente le flux de rayons gamma transmis à travers l'échantillon en fonction de la vitesse de la source, on peut calculer plusieurs paramètres dont :

- le déplacement isomérique (D.I.) mesuré par le décalage du centre de gravité du spectre par rapport à l'abscisse de vitesse nulle. Il permet de déterminer le degré d'oxydation du fer ;

- l'interaction quadrupolaire (S.Q.) donne des informations sur l'environnement de l'élément. Dans un composé paramagnétique, elle se traduit par un dédoublement de la raie Mössbauer et est mesurée par la distance entre les deux raies ;

- l'interaction magnétique donne des informations d'ordre magnétique par l'éclatement de la raie Mössbauer en 6 ou 8 composantes (spectre Zeeman).

Les premiers essais effectués sur le sulfate ferreux nous ont fourni des valeurs pour le déplacement isomérique et le couplage quadrupolaire en accord avec la littérature (11).

En analysant des encres fabriquées au laboratoire selon une recette ancienne, nous avons mis en évidence la présence d'une phase ferrique : des analyses en rayons X ont montré son caractère amorphe.

Mais les résultats les plus intéressants ont été obtenus sur des fragments du missel de Colmar : de nombreuses pages de ce manuscrit sont rongées par l'encre. Celle-ci ne possède alors aucun des constituants organiques retrouvés dans l'encre des pages intactes (fig. 1), mais elle est encore noire. C'est pourquoi nous l'avons analysée par spectrométrie Mössbauer.

- A 295 K, le spectre s'ajuste au moyen de deux doublets quadrupolaires de Fe^{3+} et de Fe^{2+} dont les déplacements isomériques et les couplages quadrupolaires sont respectivement 0,20 et 0,47 mm/sec (Fe^{3+}), 1,07 et 1,74 mm/sec (Fe^{2+}).

- A 4,2 K, on distingue trois sites, un correspondant à Fe^{2+} (raies i, j, k, l, m, n, o, p), deux à Fe^{3+} (raies g et h et a, b, c, d, e, f). La température d'ordre magnétique de la phase ferreuse a été évaluée à 20 K. L'ion Fe^{3+} apparaît sous forme d'un doublet paramagnétique et d'un spectre Zeeman. Les valeurs des paramètres calculés d'après le spectre Mössbauer (fig. 7) sont rassemblées ci-dessous

	Fe^{2+} magnétique 48 %	Fe^{3+} paramagnétique 37 %	Fe^{3+} magnétique 15 %
D. I. mm/sec.	1,285	0,41	0,42
S. Q. mm/sec.	- 2,035	0,62	0,04
H (kOe)	150		542
η	0,61		
θ	79		

avec : (H : champ hyperfin vu par le noyau
 (η : paramètre d'asymétrie du gradient de champ électrique
 (θ : angle entre le champ magnétique H et Oz, axe principal du gradient de champ électrique

Des expériences complémentaires (application d'un champ de 55 kilooersted à 4,2 K) ont montré que l'interprétation des spectres de Fe^{3+} fait intervenir un phénomène de superparamagnétisme de grains fins.

Ces premières analyses en effet Mössbauer nous ont montré que la phase ferrique appartient à des grains fins de quelques dizaines d'angströms (d'où son caractère amorphe). De plus, tous les paramètres hyperfins de l'encre du missel de Colmar étant déterminés, nous pensons pouvoir identifier les composés par des études complémentaires.

CONCLUSIONS

Nous avons vu que l'acide gallique contenu dans les encres anciennes est susceptible de se dégrader sous l'influence des facteurs biologiques ou physico-chimiques, leur effet successif pouvant amener une dégradation totale.

La mise en oeuvre des colonnes capillaires en CPV a permis une analyse plus fine des constituants des encres de manuscrits mais la détermination de l'appartenance botanique du tanin utilisée n'est pas encore possible.

Les études effectuées sur le complexe ferrogallique ne constituent qu'un début. Néanmoins, l'utilisation de l'effet Mössbauer semble très intéressante : cette technique permet en effet d'analyser à température ambiante les encres de manuscrits sans aucun prélèvement. L'identification des produits minéraux présents dans une encre ancienne peut nous aider à comprendre comment une encre métallogallique est encore noire alors qu'elle ne contient plus d'acide gallique ou uniquement à l'état de traces.

REFERENCES BIBLIOGRAPHIQUES

- (1) ARPINO (P.), MOREAU (J.-P.), ORUEZABAL (C.), FLIEDER (F.), *Gas chromatographic mass spectrometric analysis of tannin hydrolysates from the ink of ancient manuscripts (XIth to XVIth century)*, J. Chromatogr., 1977, 134, p. 433-439
- (2) BEVERIDGE (E.G.), HUGO (W.B.), *The Metabolism of gallic acid by Pseudomonas convexa* X 1, J. Appl. Bacteriology, 1964, 27 (3), p. 448-460
- (3) DAGLEY (S.), EVANS (W.C.), RIBBONS (D.), *New pathways in the oxidative metabolism of aromatic compounds by microorganisms*, Nature, 1960, 188, p. 560
- (4) DARBOUR (M.), *Les Encres métallogalliques : étude de la dégradation de l'acide gallique et analyse du complexe ferrogallique*, Université Paris VI, thèse de docteur-ingénieur, 1980

- (5) DE PAS (M.), *Les Encres noires au Moyen-Age jusqu'à 1600*, Université Paris, thèse 3e cycle, 1977
- (6) DE PAS (M.), *Etat des travaux effectués sur l'analyse des constituants des encres noires manuscrites par deux techniques : chromatographie sur couche mince et électrophorèse*, ICOM, 4e réunion, Venise, 1975
- (7) ELINANY (G.A.) and al., *Polarography of metal-gallic complexes*, J. Electroanal. Chem., 1976, 72, p. 363-369
- (8) EISSA (N.), SALLAM (H.A.), KESZTHELYI (L.), *Mössbauer effect study of ancient Egyptian pottery*, Acta Physica Academiae Scientiarum Hungaricae (Budapest), 1973, 34, n° 4, p. 337-340
- (9) FLIEDER (F.), BARROSO (R.), ORUEZABAL (C.), *Analyse des tannins hydrolysables susceptibles d'entrer dans la composition des encres ferrogalliques*, ICOM, 4e réunion, Venise, 1975
- (10) FRIEDRICH (H.), *Der Abbau von phenolischen substanzen durch Aspergillus niger*, Arch. Mikrobiol., 1956, 25, p. 297-306
- (11) GREENWOOD (N.N.), GIBB (T.C.), *Mössbauer spectroscopy*, London, Chapman and Hall, 1971
- (12) GROB (K.), *Static coating of glass capillary columns : solvent selection, column filling, solvent evaporation*, J. High Resol. Chromatogr. and Chromatogr. Commun., 1978, p. 93-94
- (13) GROB (K.), GROB (G.), GROB (K.) Jr., *Deactivation of glass capillary columns by silylation*, J. High Resol. Chromatogr. and Chromatogr. Commun., 1979, p. 31-35
- (14) J ACOB (F.H.), PIGNAL (M.C.), *Yeast tanning interactions. II Study in a tanning medium of some tannic acid hydrolysing yeasts*, Mycopathologia, 1975, 57 (3), p. 139-148
- (15) JOHANSSON (L.Y.) and al., *X-ray photoelectron and Mössbauer spectroscopy on a variety of iron compounds*, Chem. Phys. Lett., 1974, 24 (4), p. 508-513
- (16) LEWIS (J.A.), STARKLEY (R.L.), *Decomposition of plant tannins by some soil microorganisms*, Soil Science, 1969, 107 (4), p. 235-240
- (17) LOGINOVA (L.F.), MEDYNTSEV (V.V.), KHOMUTOV (B.I.), *(Acid base properties and complexing of gallic acid and its esters with iron)*, Zh. Obshch. Khim., 1972, 42 (4), p. 739-742
- (18) NAKAMURA (K.) and al., *Kinetics of the aquation of iron (III) monophenolate complexes. Absence of the acid dependent path.*, Bull. Chem. Soc. Jap., 1973, 46 (2), p. 456-459

- (19) SITARAMALAKSHMI (C.), VENKATESWARLU (C.), *Mixed ligand complex of thorium*, Indian J. Chem., 1975, 13 (6), p. 625
- (20) STAHL (E.), KARIG (F.), *Thermofraktographie zur Charakterisierung natürlicher Polyphenole, Gerbstoffdrogen und Leder*, Z. Anal. Chem., 1973, 265, p. 81-92
- (21) STANIER (R.Y.) and al., *Bacteria oxidation of aromatic compounds. III. The enzymic oxidation of catechol and protocatechuic acid to β -ketoadipic acid*, J. Bacteriol., 1950, 59, p.137
- (22) TACK (B.F.), CHAPMAN (P.J.), DAGLEY (S.), *Metabolism of gallic acid and syringic acid by Pseudomonas putida*, J. Biol. Chem., 1972, 247 (20), p. 6438-6443
- (23) TALBOT (R.), LECLERC (F.), FLIEDER (F.), *Etude de la régénération chimique des encres métalliques*, ICOM, 5e réunion, Zagreb, 1978
- (24) VARSANYI (G.) and al., *Infrared spectra of 1,2,3,5-tetrasubstituted benzene derivatives*, Acta Chim. Acad. Sci. Hung., 1977, 93 (3-4), p. 315-355
- (25) WEIGL (J.), *Über Ursachen des Tintenfrasses*, Archivalische Zeitschrift, 1974, 70, p. 101-102.

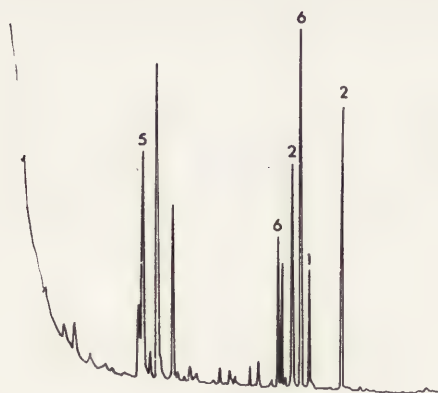


Fig. 1

MISSEL DE COLMAR XVe
non dégradé

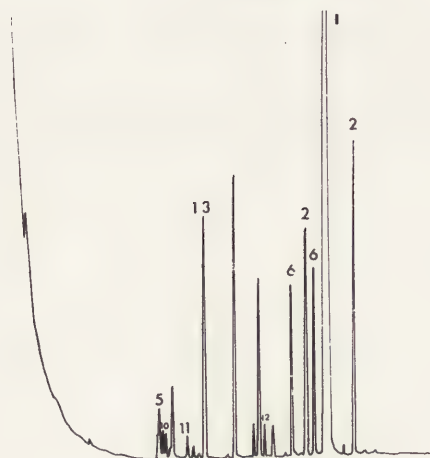


Fig. 2

NOIX DE GALLE

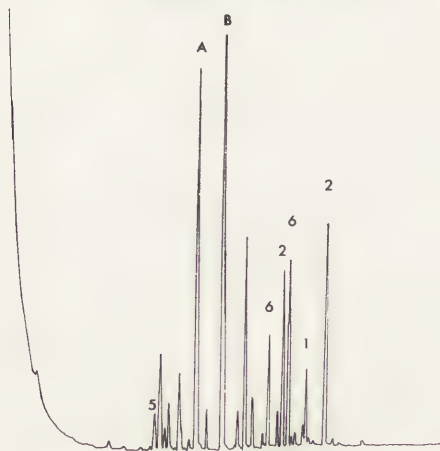


Fig. 3

NOIX DE GALLE dégradée
21 jours

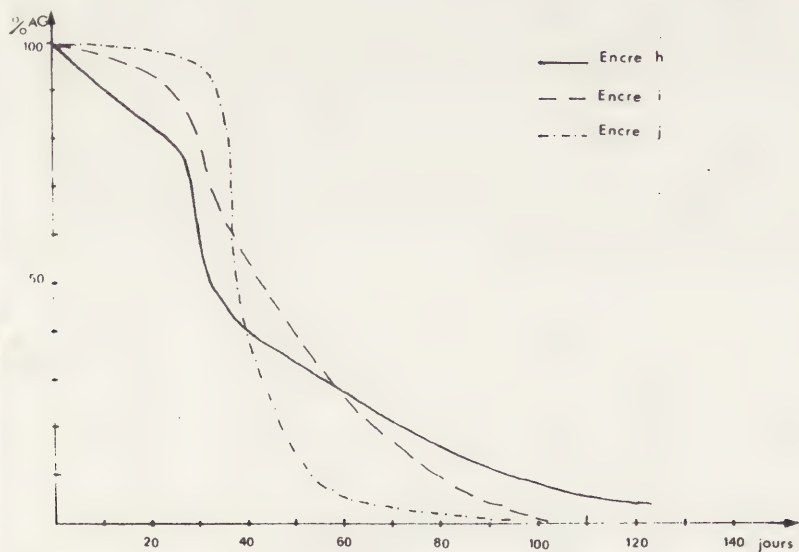


Fig. 4 : Cinétique de la dégradation de l'acide gallique dans les encre (avec milieu nutritif)

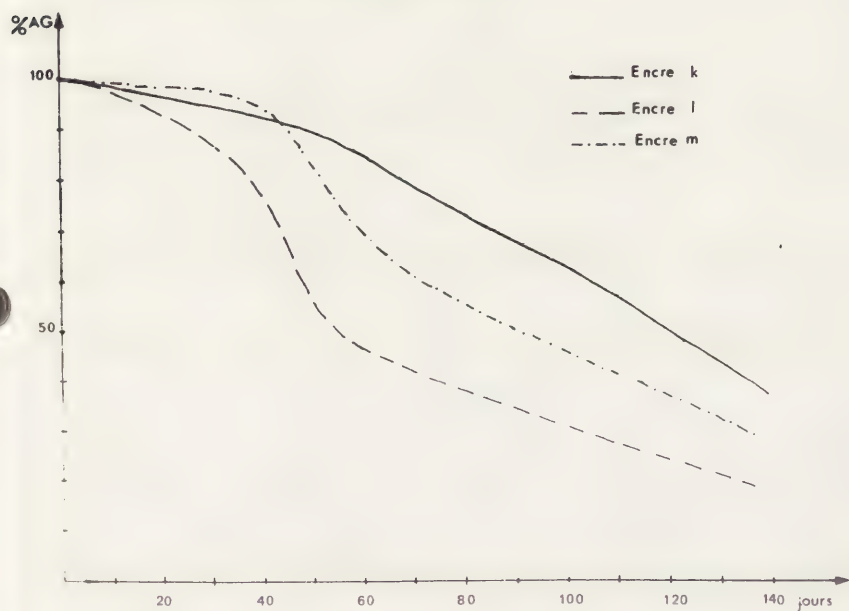


Fig. 5 : Cinétique de la dégradation de l'acide gallique dans les encre (sans milieu nutritif)

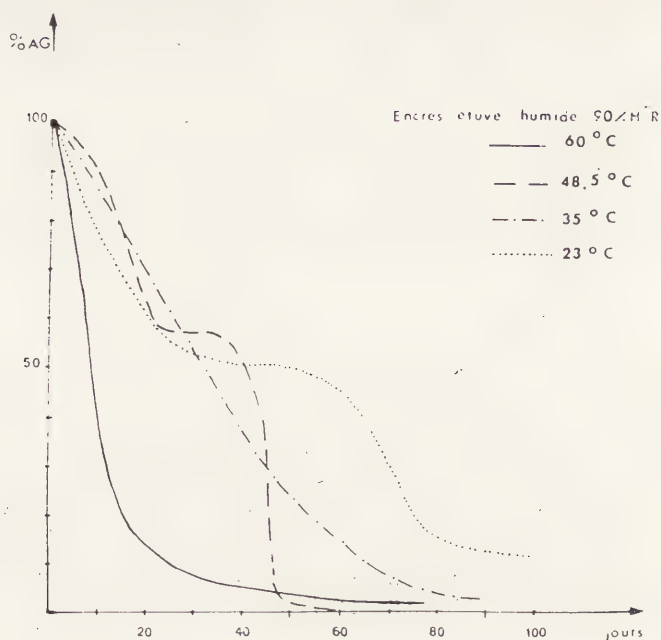


Fig. 6 : Cinétique de la dégradation de l'acide gallique dans les encres en chaleur humide

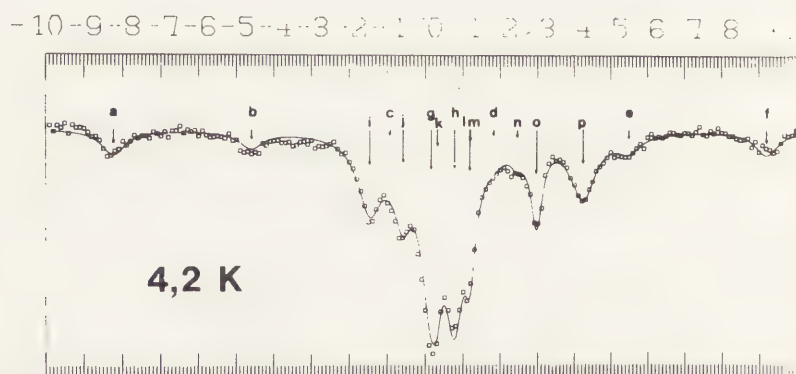


Fig. 7 : Spectre Mössbauer du Missel de Colmar (4,2 K)

81/14/4

CONCERNING THE EXPOSURE OF PAPER TO LIGHT:
DISCOLORATION OF HANDSHEETS OF KNOWN INITIAL
LIGNIN AND HOT-ALKALI-SOLUBLE CONTENT

Sang B. Lee, John Bogaard and Robert L. Feller

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents

CONCERNING THE EXPOSURE OF PAPER TO LIGHT: DISCOLORATION OF
HANDSHEETS OF KNOWN INITIAL LIGNIN AND HOT-ALKALI-SOLUBLE
CONTENT

Sang B. Lee, John Bogaard and Robert L. Feller

Center on the Materials of the Artist and Conservator
Mellon Institute
Pittsburgh, Pa. 15213
USA

Summary

Handsheets from six pulps that varied in their initial content of lignin and hot-1%-alkali-soluble matter were exposed to visible and near ultraviolet radiation from three light sources. Essentially the same behavior was observed under all three. The results indicated that a high initial content of hot-alkali-soluble matter in the cellulose is likely to lead to darkening, while lignin itself tends to bleach. The tendencies to bleach and to darken take place concurrently. It was further demonstrated that an increased percentage of lignin in the pulps will increase the rate at which hot-alkali-soluble matter is developed during exposure.

Introduction

When paper is exposed to light it can either darken or bleach. Because of the complex series of chemical reactions that occur during the degradation of paper⁽¹⁾, it is logical to assume that certain reactions will lead to bleaching, whereas others - possibly thermally activated, as suggested by Launer and Wilson⁽²⁾ - will lead to darkening. It would be useful for the conservator to be able to predict which effect will predominate in a given situation - both may be occurring at the same time.

Much of the information published in the past concerning the action of light on cellulose is of little value to the conservation scientist because the wavelength range of radiation used either was not clearly defined or contained wavelengths shorter than 313 nm, leading to photolytic reactions rather than photosensitized reactions. Moreover, the temperature of the paper samples, of major importance in photochemically initiated discoloration of paper⁽²⁾, was seldom controlled. Accordingly our laboratory initiated a series of investigations into the effects of light on papers of known composition under

carefully defined conditions of exposure.

Pure cellulose, which we shall consider as alpha cellulose, is a long chain of anhydropyranose rings linearly joined together. When oxidation takes place, perhaps the earliest stage is the formation of aldehydic or ketonic carbonyl groups from the alcohol groups in the ring. The cellulose polymer changed in this manner is often called "oxycellulose". It is generally understood that the presence of carbonyl groups can cause oxycellulose to be more susceptible than alpha cellulose to deterioration through oxidation and chain breaking reactions. The relative concentration of such oxidizable sites is commonly measured in a qualitative rather than stoichiometric manner by a determination of the "copper number", or by determining the percentage of the paper pulp soluble in hot 1% alkali.⁽⁴⁾ In many cases, a nearly linear relationship has been found between hot-1%-alkali-soluble (HAS) matter and the copper number.^(5,6) Hemicelluloses in the pulp may also dissolve in hot-1% sodium hydroxide solution, but such constituents frequently also represent easily oxidized portions of paper. Hence, in this investigation, we have used the changes in the percent HAS matter as a measure of the oxidative changes that have taken place in the cellulosic component of the handsheets. Laboratory tests not reported here confirm that determinations of the copper number would have led to the same conclusions as reached from the determination of HAS matter.

Composition of the Papers

Handsheets were made from pulps kindly provided by various manufacturers or from pulps chemically modified in the laboratory, described in Table I. The groundwood pulp, sample GP, was chemically modified to alter the proportions of initial lignin and HAS matter. To reduce the lignin content, the GP pulp was treated for four hours with sodium chlorite and glacial acetic acid at 70°C, then neutralized and washed to give a sample labeled as 4HC. Portions of this were then either washed with sodium hydroxide or reduced with sodium borohydride, yielding pulps designated as 4HC NaOH and 4HC SBH, respectively. Thus, six pulps containing various initial amounts of lignin and HAS matter were prepared from which to make handsheets (Table I). The cold extraction pH of all handsheets was between 5.5-6.0.

Light Sources Used for Exposure

Three different light sources were used to determine if there would be variations in the results owing to differences in sample temperature and spectral distribution of the irradiance: (a) a bank of six General Electric High-Output (HO) "daylight" fluorescent lamps, (b) a bank of six fluorescent BLB blacklights, and (c) an Atlas 600WRC xenon-arc fadeometer with pyrex filter. The irradiance on the samples under the three lamps in the ultraviolet and visible spectral regions is given in Table II. These data are presented primarily to show the percentage of ultraviolet emitted by the various sources.

Both types of fluorescent lamps were mounted about 3 1/2" above

the samples in a room maintained at 50% relative humidity (RH) and 70°F (21.1°C). The temperature of the handsheets reached about 24°C. In the 600WRC fadeometer, the air was maintained at 31°C ($\pm 1.0^\circ$) and 27% RH; the black-panel temperature reached 65°C. Because the ranking of six different papers according to the degree of darkening or bleaching was essentially the same under all three sources, we believe that the experimental conclusions were not seriously affected by differences in the temperature and humidity under the different sources.

Discoloration

The degree of lightening (bleaching) or darkening was measured in terms of the change in post-color number (p.c. no.), calculated by subtracting the K/S value of the exposed samples at 457 nm from the K/S value of the sample initially, and multiplying by 100. The value for K/S is obtained from the reflectance, R, of a stack of six sheets of the sample papers, according to the relation $K/S = (1-R)^2/2R$.⁽³⁾ A plus value for p.c. no. indicates darkening; a minus value, bleaching, regardless of the initial reflectance. The changes in p.c. nos. for the six papers following exposure to "daylight" fluorescent lamps are shown in Figure 1. The ranking of the various papers was essentially the same following exposure under the other two light sources and, hence, data obtained with the other sources will not be presented.

We see that three of the papers darkened significantly, one slightly, one scarcely changed at all, and one bleached considerably. The latter was made from the unbleached pulp, UBP, and had a significant amount of lignin present along with a low initial concentration of HAS matter. Based on additional tests that will not be reported at this time, we presently believe that, among the numerous chemical processes that must be occurring during exposure to visible and ultraviolet radiation, lignin, a dark-colored material, tends to bleach. Further studies will be conducted to confirm this conclusion.

What caused greater darkening in some of these papers relative to others? A graph of the initial rate of darkening (the linear slope between the initial and the 70-hour data points in Figure 1) plotted against the initial percentage of HAS matter in the pulps indicates the two are related (Figure 2). In other words, the rate of darkening induced by visible and ultraviolet radiation seems to be related to the amount of HAS matter or oxycellulose initially present in papers that have not previously been thermally aged. Data obtained under the other sources confirm this relationship.

Influence of Lignin on the Development of Hot-Alkali-Soluble (HAS) Matter

One can measure not only the darkening of the sheets with time of exposure, but also the development of an increased amount of HAS matter (Figure 3). An initial rate of development of HAS matter can also be calculated from the initial HAS content and the percentage determined

at 160 hours. When the initial rates of formation of HAS matter (representing oxycellulose) under each of the types of illumination are plotted against lignin content, the set of curves shown in Figure 4 is obtained. A logarithmic plot has been used in order to cover the wide range in lignin content. The inference that can be drawn from these data is that, as the amount of lignin initially present increases, the rate at which paper develops HAS matter upon exposure to visible and near-ultraviolet radiation also increases.

Discussion

From consideration of the results of these initial investigations of the changes that occur in paper during exposure to light, we believe that we are confronted with at least two principal chemical processes which result in conflicting evidence of change: the darkening taking place owing to the presence of oxycellulose (HAS matter), and the bleaching of the lignin itself, the presence of which also leads to the creation of more HAS matter. Thus, one must realize, the fact that paper has exhibited only a minor change in color does not indicate that negligible chemical changes have taken place. Instead, the color changes may have nearly cancelled one another. The case in point is the comparison of the two papers in Figure 1 exhibiting little change in color, samples 4HC NaOH, which darkened only slightly, and the bleached pulp, BP, which changed scarcely at all. The amounts of lignin and HAS matter initially present in the BP pulp were low, so that its lack of marked change is not surprising. However, sample 4HC NaOH contains nearly the same amount of lignin as sample UBP, which bleached significantly; one might expect that bleaching would have also occurred in sample 4HC NaOH. That it did not appear to undergo the expected bleaching can be assumed to be due to the darkening generated by the higher initial concentration of HAS matter. The result was practically no change in color during exposure.

Conclusions

Our introductory investigation into the photochemical deterioration of papers having a known content of lignin and hot-alkali-soluble (HAS) matter has helped to pinpoint possible causes of darkening and lightening of papers and to demonstrate that both processes may be occurring simultaneously during exposure. The results further support the findings of Reine and Arthur⁽⁷⁾ who showed that exposure to near-ultraviolet radiation tends to generate oxycellulose, that is, cellulose with increased carbonyl groups. The introduction of such groups in the cellulose chain can be followed by measurement of the increased hot-alkali-soluble (HAS) matter (Figure 3). The investigation further demonstrates that increased amounts of lignin in paper tend to increase the rate at which HAS matter is generated upon exposure to light (Figure 4). The presence of considerable carbonyl content in the cellulose chain, and possibly the presence of hemicellulose components in the pulps - represented by the HAS matter initially present - tends to cause paper to darken on exposure to near-ultraviolet and visible

radiation (Figures 1 and 2). In contrast, evidence suggests that the color of lignin itself tends to be bleached.⁽⁸⁾

Because the ranking of test papers was not changed under the three sources of illumination used in these experiments, and because a similar response to lignin content, seen in Figure 4, was obtained under all three sources, we suggest that the photochemical deterioration of paper induced by near-ultraviolet and visible radiation can be conveniently studied in the laboratory with the use of "daylight" fluorescent lamps, fluorescent BLB black lamps, or a xenon-arc fadeometer with pyrex-glass filters, providing the sample temperatures are kept as low as conveniently possible. It seems reasonable to assume that the photochemical response of the test papers under the bank of "daylight" fluorescent lamps used here would be similar to the chemical and physical changes that would occur in a gallery under diffuse daylight through window glass. Future experiments, continuing the lines of investigation developed here, are in progress.

Acknowledgment

This investigation was undertaken with the support of a grant from the National Museum Act. The authors gratefully acknowledge the assistance of David Encke and Mary Curran in calibrating the light sources and providing comparative information on the rates of fading of the ISO R105 blue-wool fading standards.

References

1. Arney, J. S. and Chapdelaine, A. H., "A kinetic study of the influence of acidity on the accelerated-aging of paper", American Chemical Society, Advances in Chemistry Series, No. 194 (1981), in press.
2. Launer, H. F. and Wilson, W. K., "Photochemical stability of papers", Journal Research National Bureau of Standards, 30 (1943), 55-74.
3. Tongren, J. C., "A reflectance method for the study of discoloration of artificially aged papers", Paper Trade Journal, Technical Association Section, 107, No. 8 (1938), 34-42.
4. Tappi Standard T212 05-76, "One percent sodium hydroxide solubility of wood and pulp", (1976).
5. Glibbens, D. A., Geake, A. and Ridge, B. P., "The chemical analysis of cotton. The action of hot dilute sodium hydroxide solutions on modified cotton cellulose", The Journal of the Textile Institute, XVIII (1927), T277-T282.
6. Meller, A., "The hot alkali stability of chemically modified cellulose fibers", Australian Pulp and Paper Ind. Tech. Proc., 7 (1953), 263-315.
7. Reine, A. H. and Arthur, J. C., Jr., "Photochemistry of cotton cellulose. The direct action of near ultraviolet light on purified fibrous cotton cellulose", Textile Research J., 40 (1970), 90-92.
8. Additional evidence indicates that discoloration that is the result of the thermal aging of pulps, which may possibly be colored components of gamma cellulose, also tends to bleach.

TABLE I
Characteristics of Various Paper Samples Prepared in
the Laboratory (Before Exposure to Light)

Sample Designation	Description	Initial Reflectance at 457 nm	Lignin Content (%)	Initial Hot-1%-Alkali Solubility (%)	Copper Number
BP	Bleached Pulp (50% Hardwood Kraft/50% Softwood Kraft)	83.6	0.24	5.0	0.5
UBP	Unbleached Pulp (50% Hardwood Kraft/50% Softwood Kraft)	30.8	4.4	3.7	0.6
GP	Unbleached Groundwood Pulp	57.0	29.1	15.6	2.9
4HC	4 Hours' Chloriting of GP	57.3	8.1	30.8	5.2
4HC NaOH	4 Hours' Chloriting of GP; Hot-1%-NaOH Extraction	36.1	4.0	8.3	0.97
4HC SBH	4 Hours' Chloriting of GP; Sodium Borohydride Reduction	53.3	7.7	29.8	4.3

TABLE II
Irradiance from Different Light Sources ($\times 10^{-3}$ w/cm²) as Measured by the IL700 Radiometer

Light Source	Ultraviolet Energy (310-392 nm)	Visible Energy (400-750 nm)	Total Energy (257-750 nm)	Measurement Distance from Source (Inches)
G.E. Fl. Black-light F40 BLB	4.13 (86%)	.77	4.90	3.5
Fl. "Daylight" High Output	.228 (3.8%)	5.70	5.928	3.5
Xenon-Arc Fadeometer* Pyrex/Pyrex Filters	13.775** (6.3%)	203.49***	217.265****	11.6

*Measurements obtained from Atlas Electric Devices Inc. catalog multiplied by 1.9 (factor for inner ring especially installed). **Irradiance from 340-400 nm. ***Irradiance 400-750 nm. ****Irradiance from 340-750 nm.

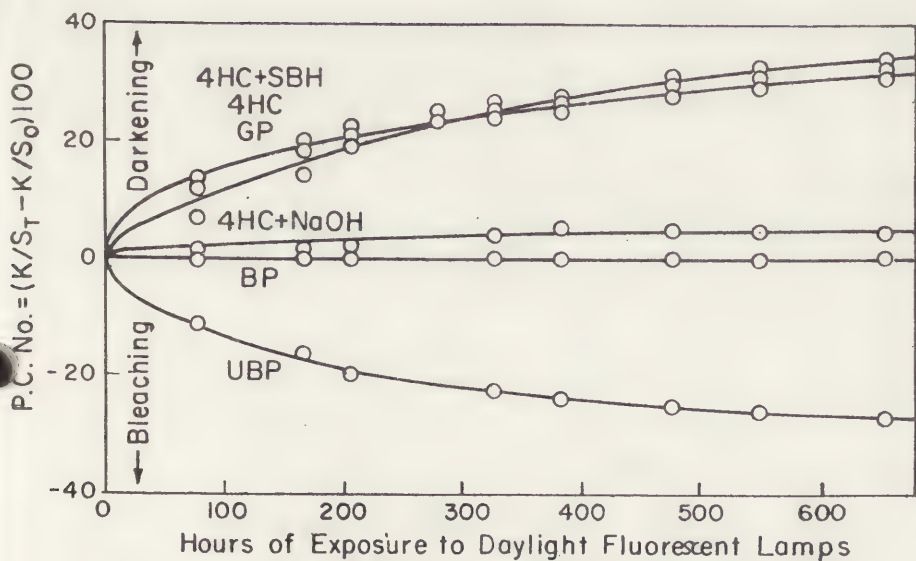


Figure 1

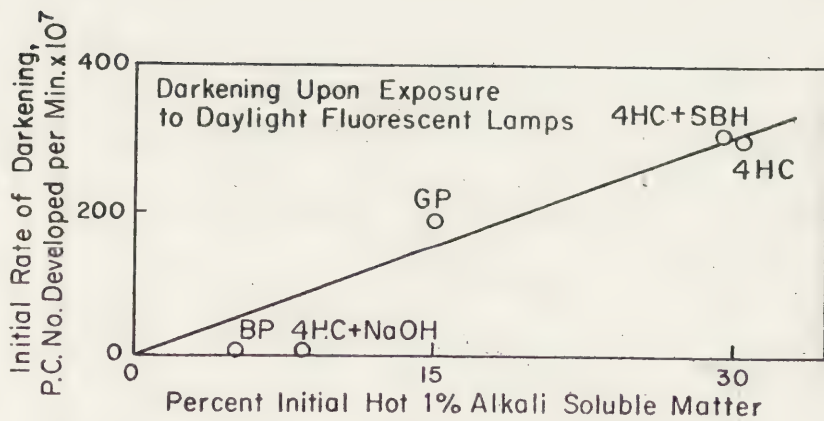


Figure 2

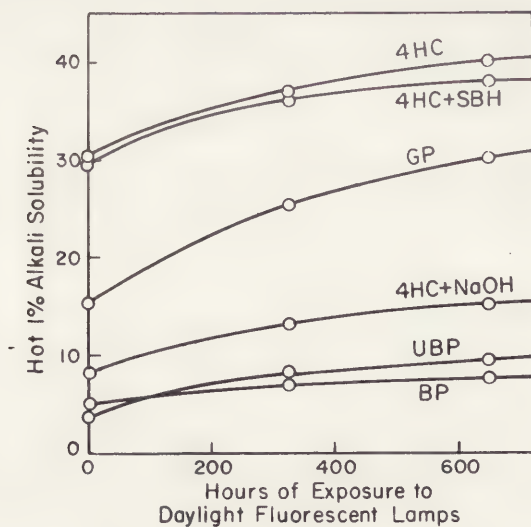


Figure 3

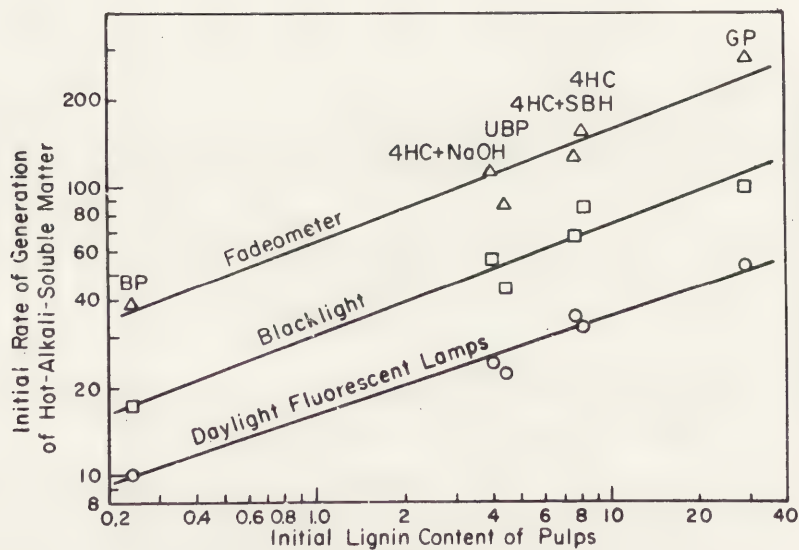


Figure 4

81/14/5

THE FORECASTING OF THE LONGEVITY OF PAPER,
COMPARISON OF METHODS

M.G.Blank, D.M.Flyate and E.M.Lotsmanova

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



THE FORECASTING OF THE LONGEVITY OF PAPER, COMPARISON OF
METHODS

M.G.Blank, D.M.Flyate and E.M.Lotsmanova

M.E.Saltykov - Shchedrin State
Public Library
18 Sadovaja Street
191069 Leningrad
USSR

The method of the evaluation of permanence and durability of paper based on the kinetic concept of strength was used for the definition of properties of paper which is intended for extensive use and handling. The method showed good results in the forecasting of the longevity of industrially-made paper samples. Some data have been received which make it possible to compare paper service life predicting methods such as thermal analysis, Arrhenius equation and the kinetic concept of strength.

The intensive development of investigations in the field of the prevention of paper from aging has resulted in the creation of permanent and durable kinds of paper, the experimental industrial production of which is carried out at paper-making factories of different countries. With the production of such kinds of paper there arises the necessity of the evaluation of their longevity.

The forecasting of the longevity of paper continues to be one of the topical subjects of the present-day researches. The use of artificial heat aging for these purposes has some essential drawbacks. The problem appears to be more difficult with the use of synthetic kinds of sizing in the composition of paper instead of rosin and alum, the former interacting with cellulose and providing the formation of new bonds, the high temperature affecting it greatly. Hereupon there arise conditions

permitting the simultaneous proceeding of competitive reactions of destruction and structurization, making it difficult the application of the laws of chemical kinetics to paper aging.

In this work the evaluation of permanence and durability was carried out for five kinds of industrially-produced paper, the data of their composition being shown in Table I. All these kinds of paper were made as durable, while the sixth one, put in the table for comparison, is the usual industrially-made kind of paper for writing.

The longevity of paper was evaluated on the basis of accepted methods with the use of the activation Arrhenius equation, the kinetic concept of strength and thermal analysis.

Table I

The composition of the kinds of paper tested

No	Kind of fibres	Kind of sizing	Kind of filler
I	Softwood sulphate, hardwood sulphate	Cyclopal KE produced in FRG	Clay
2	"	Basoplast 824I	"
3	"	Tinoresin produced by Zyba-Teigy, Switzerland	"
4 ^x)	Softwood sulphate, cotton cellulose	Cyclopal KE, Na CMC	Calcium carbonate
5	Cotton cellulose	Aquapel	"
6	Softwood sulphite	Rosin, alum	-

^x) Trilon is introduced into the paper

I. The evaluation of permanence and durability of paper with the help of the activation Arrhenius equation. The description of the technique for using the method is shown in some works [1, 2].

The artificial aging was carried out in tightly shut glass pipes, the constant humidity being kept in the closed volume at the temperatures of 60, 75, 90, 105°C, in the course of 6, 12, 18, 24, 30 days. For the evaluation of the change of properties the value of folding endurance, bleaching degree and copper number were used.

In all cases the diagrams of the logarithm of the change of properties as a function of time of aging have the non-linear character. At the first stages of aging an increase of paper strength takes place. At high temperatures the leaped change of properties increases. The main cause of non-linearity seems to be explained by the presence of synthetic sizing materials. The calculation of the values of rate constants and activation energies of processes taking place while aging which were obtained from the linearized functions with the use of least squares method has showed that the values of the activation energy are too low (30 - 70 KJ/mol), but this does not correspond to the well-known limits.

The technique of carrying out the experiments takes much time, it requires the use of artificial heat aging, the conditions of which are not worked out completely. The essential drawback of the method is the impossibility of taking into consideration the initial mechanical strength of the paper, which undoubtedly plays a great role in the natural conditions of usage.

II. The next step in the work was the evaluation of the permanency and durability of paper with the use of artificial aging under the action of mechanical load. The theoretical principles of the method were formulated in the report at the 5th Triennial Meeting ICOM [3].

As an example the calculation of the value of the activation energy for the process of destruction (U_0) of paper No 4 (Table I) on the basis of the kinetic

concept of strength is shown below.

The formula for calculation found as the result of modification of the main equation of longevity

$$\tau = \tau_0 \exp \frac{U_0 - \gamma \sigma}{RT} \quad (1)$$

has the form of

$$\lg \tau_1 = \lg \tau_0 - \lg I_0 \left(\frac{\gamma \sigma_0}{2RT} \right) + \frac{U_0}{2.3RT} - \frac{\gamma \sigma_0}{4.6RT} - \frac{\gamma}{2.3R} \sigma_{st}, \quad (2)$$

where

τ_1 - time period from the beginning of loading to the specimen rupture, s ;

τ_0 - period of atomic oscillation in molecule, s ;

I_0 - Bessel's function with an imaginary argument ;

γ - coefficient characterizing the degree of nonuniformity in microstress distribution in the solid under test, $\frac{\text{J} \cdot \text{m}}{\text{g} \cdot \text{mol}}$;

σ_{st}, σ_0 - static and dynamical stresses which the material experiences, Pa ;

R - universal gas constant, $\frac{\text{J} \cdot \text{g} \cdot \text{mol}}{\text{K}}$;

T - temperature, K ;

Example of calculation

A. Initial parameters of the paper under test :

thickness (h), m - 9×10^{-5} ;

strip width (b), m - 1.5×10^{-2} ;

cross section area (s), m^2 - 13.5×10^{-7} .

B. The determination of the value of the folding endurance of paper at 5 loads, the calculation of the time period of double folds until the sample rupture (the time period of one double fold is 0.5 s), the calculation of the value of the static stress according to the formula

$$\sigma_{st} = \frac{F_1}{s}, \quad (3)$$

where F_1 - the value of the load, N .

The experimental and the calculated indices of the sample of the paper are shown in Table 2.

Table 2

Name of parameter	Values of paper indices				
F_i, N	6.86	7.84	8.82	9.8	11.76
Folding endurance the number of double folds	572	403	384	238	99
Time period of one test until the rupture (τ_i), s	286	201.5	192	119	49.5
$\lg \tau_i$	2.46	2.3	2.28	2.08	1.69
σ_{st}	50.8	58.1	65.3	72.6	87.1

C. According to the experimental data a diagram of relation $\lg \tau = f(\sigma_{st})$ is drawn which is a straight line for the paper under test.

D. Using the data of point B with the help of the least squares method the equation (2) is solved in the form:

$$\lg \tau_i = a + b \sigma_{st}$$

and the values are determined:

$$a = 3.55 \quad \text{and} \quad b = 127.7 \times 10^{-5}$$

E. The value of dynamical stress is found by determining the strength leading to the rupture of the paper strip by stretching at a constant speed on the tensile tester, this value being admitted to correspond to the maximum value of the dynamical loading at the fold testing, as the value of the maximum stress at the cycle loading for paper folding can't be higher than the stress value at the rupture by stretching.

The value of the strength leading to the rupture of the paper strip -breaking strength (F_2) is 61 N, and the value of dynamical stress (σ_c) is $453.3 \times 10^{-5} \frac{N}{m^2}$

F. The value of the activation energy of the process of paper destruction (U_0) is determined according to the formula (2), for the paper under test it is equal to $139.7 \frac{\text{K J}}{\text{mol}}$.

J. The activation energy of the process of paper destruction under load (U) is found by the formula :

$$U = U_0 - \gamma(\sigma_{st} + \sigma_d) \quad , \quad (4)$$

where

$$\sigma_d = \frac{\sigma_c}{2} \quad (5)$$

and σ_{st} is taken by the load 9.8 N .

The value (U) for paper No 4 is $102.3 \frac{\text{K J}}{\text{mol}}$.

The values of activation energy of the process of paper destruction for the rest of the kinds of paper were calculated in the same way. The results obtained are compiled in Table 3 .

Table 3

Kinetic parameters of paper samples

Name of parameter	Numbers of paper samples					
	I	2	3	4	5	6
U_0	141.8	133.7	101.2	139.7	154.0	134.9
U	101.3	98.2	80.7	102.3	110.0	96.1
E	144.2	149.6	130.2	166.2	242.0	-
The longevity of paper samples on the basis of (U) as compared with that of the sample No6, number of times	8.4	2.4	0.16	12.6	300	1

We consider that it is the value of the activation energy of the process of paper destruction under load U , that serves as a criterion of stability and resistibility to all influences upon it in the process of storing and using.

III. The thermogravimetical analysis of paper samples was carried out on the derivatograph OD-102 "MOM" firm (Hungary). The calculation of the values of the activation energy of the process of paper thermal destruction E was carried out according to the work [4] by the Horowitz-Metzger method [5] . The results of the tests are shown in Table 3. The method permits to get varied information of high accuracy about a paper sample under test within a short period of time, but it requires special instrumentation. The values of the activation energy of the process of paper destruction E are comparatively higher than the values of U_0 , for they reflect the phenomenon of thermal destruction at pyrolysis.

The analysis of all data obtained permitted to find out most durable and permanent kinds of paper, the samples No 4 and 5 appearing to be such, the minimum stability in all cases being shown by the No 3 .

For evaluation of the stability level of the experimental kinds of paper, their comparing with the widely-used kind of writing paper " Pischaya No I. " (sample No 6) was made on the basis of the values of the activation energy of the process of paper destruction under the load U . The results expressed in the number of times of durability increase in comparison with the paper No 6 are shown in Table 3. The paper composed of cotton fibres and containing Aquapel as a sizing materials and calcium carbonate as a filler, appeared to be 300 times more durable, than the usual writing paper.

Thus, the work performed has shown that the method based on the artificial aging under the action of mecha-

nical load gives sufficiently accurate results, permits to evaluate the permanence and durability of paper containing synthetic materials. It is based on the measurement of the folding endurance value which is one of the most sensitive indices of the change of paper properties in the process of aging. The calculation is made also with the use of the breaking strength index of paper. All the necessary measurements and calculation could be carried out quickly in the course of one working-day.

References:

1. Browning R.L., Wink W.A. Studies on the permanence and durability of paper. - "TAPPI", 1968, vol. 51, No. 4, p. 156 - 163.
2. Иванов Г.А., Фляте Д.М., Шульман И.С. О кинетике термического старения волокон целлюлозы. В кн.: Вопросы долговечности документа. Л., "Наука", 1973, с. 5 - 11.
3. Blank M.G. Prediction of the service life of the paper containing polymeric adhesives. - ICCM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978, 78/I4/6.
4. Бланк М.Г., Сазанов Ю.Н. Использование методов термоанализа для определения стабильности бумаги различной композиции. - "Теория и практика сохранения книг в библиотеке", Л., 1974, вып. 6, с. 34 - 56.
5. Horowitz H.H., Metzger G.A. A new analysis of thermogravimetric traces. - "Analytical chemistry", 1963, vol. 35, No 10, p. 1464- 1468.

81/14/6

EFFET DE LA POLLUTION ATMOSPHERIQUE SUR LE
CUIR ET LE PARCHEMIN

Claire Chahine et Martine Leroy

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Documents graphiques et
photographiques

EFFET DE LA POLLUTION ATMOSPHERIQUE SUR LE CUIR ET LE PARCHEMIN

Claire Chahine et Martine Leroy

Centre de Recherches sur la Conservation des Documents
Graphiques
36 Rue Geoffroy-Saint-Hilaire
75005 Paris
France

Résumé

Pour simuler l'effet de la pollution atmosphérique sur le cuir et le parchemin, un caisson expérimental dans lequel on peut faire varier la température, l'humidité relative et contrôler l'admission de gaz polluants a été construit. Des cuirs y ont été soumis à l'action de l'anhydride sulfureux en présence de catalyseurs et d'oxydant (le peroxyde d'azote) et à forte humidité. Des détériorations ont pu être constatées au bout de cinq semaines.

Parallèlement à cette étude, nous avons suspendu des échantillons dans un site particulièrement pollué, la ville de Rouen et des prélèvements seront effectués à des intervalles de temps réguliers. Une corrélation pourra être ainsi établie entre une altération artificielle en laboratoire et une altération "naturelle" in-situ.

Les problèmes posés par la conservation des oeuvres d'art soumises à la pollution atmosphérique ne sont pas nouveaux puisqu'au XVII^e siècle on parlait déjà de "l'action corrosive de la fumée de charbon" et que l'on avait constaté des dégâts provoqués par "l'air, l'humidité, le soleil et la lune". Le charbon dont Marco Polo introduisit l'usage en Europe à la fin du XIII^e siècle devait être à l'origine des méfaits de la pollution, bien que son "odeur de soufre" en ait retardé de quelques siècles l'utilisation courante. Mais les problèmes ne sont cependant devenus aigus qu'à partir du XIX^e siècle, avec l'essor de l'industrie.

De nombreux travaux ont mis en évidence l'importance de cette pollution dans la détérioration des matériaux les plus divers ; le cuir utilisé pour la reliure est particulièrement vulnérable. Une visite en octobre 1977 dans différentes bibliothèques de la région rouennaise, un des sites les plus pollués de France, nous a permis de constater l'état désastreux dans lequel se trouvent certaines reliures conservées dans des endroits très exposés, en particulier les Archives départementales installées au centre de la ville. La bibliothèque Flaubert, abritée par la mairie de Canteleu, a

également retenu notre attention : les rayonnages de livres y sont disposés devant des fenêtres s'ouvrant sur un port industriel de la Seine et de surcroît sont exposés plein sud. Les reliures sont dans un stade avancé de dégradation ; par contre, le papier n'est pas abîmé, les livres étant bien serrés les uns contre les autres.

Il était donc important de mettre en oeuvre des moyens de lutte pour protéger efficacement les milliers de reliures qui sont en péril, ou qui le seront tôt ou tard, si le niveau de la pollution atmosphérique reste aussi élevé. Avant d'aborder la protection elle-même, il faut auparavant définir les facteurs qui provoquent la dégradation, en comprendre les mécanismes et la reproduire expérimentalement. A cet effet, nous avons construit au laboratoire un caisson pour simuler cette pollution. Nous comparerons les effets obtenus lorsqu'on y soumet des cuirs et des parchemins, à ceux constatés sur des échantillons exposés dans plusieurs sites de la ville de Rouen.

LES AGENTS DE LA POLLUTION ATMOSPHERIQUE

Ce sont, d'une part les particules en suspension, d'autre part les gaz corrosifs qui se trouvent mêlés aux composés de l'air. En outre, la vapeur d'eau à forte concentration, et les radiations solaires, favorisent l'interaction des différents polluants entre eux.

L'anhydride sulfureux est l'un des polluants gazeux les plus agressifs ; il est présent dans tous les types d'atmosphères urbaines et industrielles et il est tenu par tous les auteurs comme le principal responsable des dégâts causés aux matériaux.

Après son émission, il tend à s'associer avec les particules solides et liquides suspendues dans l'air, devenant ainsi un constituant des aérosols, avant d'être dispersé par les vents. Cependant, une partie est oxydée en anhydride sulfurique SO_3 qui réagit avec la vapeur d'eau pour former des brouillards d'acide sulfurique H_2SO_4 , redoutable agent de détérioration pour les matériaux.

1. Oxydation de SO_2 dans l'atmosphère

Le phénomène d'oxydation est extrêmement complexe et dépend des conditions météorologiques. Plusieurs mécanismes ont été proposés et ils ont été soumis à des expériences et vérifications en laboratoire. On distingue ainsi :

- une *oxydation photochimique en milieu gazeux* provoquée par l'action des radiations ultra-violettes sur l'ozone ou les hydrocarbures insaturés en présence d'oxydes d'azote. Un grand nombre de radicaux et de réactifs intermédiaires qui sont ainsi formés sont capables d'oxyder SO_2 en SO_3 (3,4) ;

- une *oxydation catalytique en milieu aqueux* produite grâce à certaines substances présentes dans les aérosols jouant le rôle de catalyseur (Fe, Pb, Mn, Cu ...). Elle est très rapide dans le panache des fumées où les concentrations en SO_2 et en particules sont relativement élevées (2). FREIBER (6) a mis en évidence que la vitesse d'oxydation catalytique en présence de fer croît avec l'augmentation de l'humidité relative et décroît avec l'augmentation de la tempé-

ture. JUNGE et RYAN (9) ont étudié l'effet du pH sur la vitesse de la réaction.

Dans le mélange complexe que sont les atmosphères polluées, la transformation de SO_2 est le résultat de plusieurs de ces mécanismes pouvant se produire simultanément, certains pouvant cependant être prédominants dans des conditions atmosphériques spécifiques.

2. Action de SO_2 sur les cuirs

Déjà au siècle dernier, l'attention était attirée sur l'action corrosive des gaz produits lors de la combustion incomplète du pétrole des lampes. De nombreux travaux ont montré, grâce à des analyses réalisées sur des reliures détériorées, que les parties les plus abîmées étaient celles qui contenaient les plus grandes quantités de sulfates ; INNES (8) en déduit une action certaine de SO_2 de l'atmosphère. Ayant constaté d'autre part que, dans les mêmes conditions de conservation, certaines reliures résistent mieux, il en conclut que celles-ci contiennent des substances capables de les protéger.

FREY et BEEBE (7) en 1940 élaborèrent une "chambre à gaz" pour le vieillissement artificiel du cuir, dans laquelle ils faisaient brûler du fuel contenant du soufre ; l'expérience était réalisée à 45°C et à une humidité relative de 37 à 55 % ; les auteurs ont observé une altération du cuir au bout de 12 semaines. BEEBE, FREY et HANNIGAN (1) ont établi une corrélation entre un séjour de 18 semaines dans cette chambre d'exposition et un vieillissement naturel de 12 à 19 ans.

ETUDE EXPERIMENTALE

En laboratoire

1. Choix des facteurs simulant la pollution

Nous avons construit au laboratoire un caisson expérimental en nous référant au montage précédemment utilisé par C. FIAUD (5). Le schéma de l'appareillage figure en fin d'article. La source de polluants est fournie par des tubes à perméation dont la vitesse de désorption des gaz est fonction de la température et du débit de l'air qui les traverse.

Dans un premier temps, nous avons expérimenté l'effet de l'anhydride sulfureux seul, puis son effet en présence de catalyseurs. La vitesse d'oxydation de SO_2 en SO_3 , même à forte humidité, étant trop lente, nous avons ajouté l'action d'un oxydant, le peroxyde d'azote NO_2 .

La réaction entre SO_2 et NO_2 est intéressante car elle provoque la formation d'acide sulfurique par l'intermédiaire de différents composés dont le sulfate acide de nitrosyle NOHSO_4 (12). Bien que le processus d'oxydation du SO_2 soit différent de ceux décrits précédemment, la réaction aboutit à la formation du même agent de détérioration, l'acide sulfurique. Nous la retiendrons dans notre expérimentation.

Des traitements complémentaires, hors du caisson, en milieu humide et sous les radiations UV ont été ultérieurement effectués.

Les gaz polluants

Des tubes de perméation type Metronics ont permis de travailler :

- pour le SO_2 , à des doses de 7 à 13 ppm, correspondant à une concentration environ 10 fois plus grande que ce qu'on peut relever dans une atmosphère polluée ;
- pour le NO_2 , à des doses de 2 à 5 ppm.

Les concentrations en polluants sont vérifiées par l'analyse de l'air à l'entrée du caisson. On effectue un dosage de l'acidité totale $\text{SO}_2 + \text{NO}_2$ après balayage des gaz dans l'eau oxygénée (10), puis un dosage seul, selon la méthode de SALTZMAN (11). Par différence, on obtient la concentration en SO_2 .

A la sortie du caisson, ces mêmes dosages permettent de contrôler les concentrations en SO_2 et NO_2 résiduelles.

La température et l'humidité

Les essais ont été réalisés à 25° et 30°C avec des humidités relatives variant de 75 à 95 %.

Les catalyseurs

Des sels de fer, de cuivre et de sélénium ont été utilisés ; ils sont entraînés par le passage de l'air chargé de gaz polluants et restent ainsi sous forme de particules en suspension.

Les traitements complémentaires

Les échantillons pollués ont été soumis aux radiations ultraviolettes* et à l'humidité** afin d'accélérer le phénomène de détérioration après la fixation d'acide sulfurique.

2. Analyses permettant de suivre la dégradation

Les premiers traitements destinés à déterminer les conditions expérimentales optimales ont été effectués sur de petits échantillons de cuir de veau. De ce fait, seule une analyse chimique partielle a été réalisée. L'analyse mécanique nécessitant de grandes quantités de cuir, car les résultats sont très dispersés, sera utilisée ultérieurement.

* produites par une lampe à décharge à haute pression dans la vapeur de mercure émettant dans le visible et le proche UV (365 nm). Les échantillons ont été exposés sur les deux faces.

** humidité : nous avons suspendu nos échantillons dans une étuve réglée à 30°C, 95 % H.R.

Les tests suivants ont été retenus :

- pH et indice de différence (*norme Afnor G 52-214*)
- matières solubles (*norme Afnor G 52-205*)

- dans les matières solubles, nous dosons d'une part les sulfates par gravimétrie de Ba SO_4 ; ceci, en relation avec le pH, est une estimation de l'acide sulfurique qui peut se fixer sur le cuir. D'autre part, nous dosons, par la méthode Kjeldahl, la quantité de composés azotés ; cette analyse est une indication de la dégradation du collagène qui est une protéine insoluble dans l'eau. Le dosage comprend deux étapes : une distillation directe sur magnésie, ce qui correspond aux sels d'ammonium, suivie d'une minéralisation et d'un déplacement de l'ammoniac, donnant la fraction d'azote protéique,

- température de rétraction T_R (*norme Afnor G 52-012*)

3. Résultats expérimentaux

Effet de SO_2 seul

Les échantillons ont été soumis à 25°C, 95 % H.R. à des concentrations en SO_2 de 5 à 13 ppm pendant des temps variant de une semaine à un mois. Aucune modification des cuirs n'a été constatée, sauf une diminution du pH de 0,5 unité environ.

Effet de SO_2 en présence de catalyseurs

Nous avons utilisé du chlorure ferrique et un mélange de sulfate de cuivre et de sélénium.

Des traitements de une semaine à un mois, à 25°C et à 30°C, à 95 % H.R. et à des concentrations de 5 à 13 ppm en SO_2 n'ont produit aucune détérioration des cuirs, si ce n'est là encore une diminution du pH dans les mêmes proportions que dans les essais précédents.

Effet de SO_2 + NO_2

Les résultats sont rassemblés dans le tableau 1. Tous les pH diminuent de façon considérable. On constate en outre que, dans l'ensemble, l'effet sur les cuirs augmente :

- avec la concentration en gaz polluants ; c'est ainsi que leur action est pratiquement nulle à 7 ppm de SO_2 et 2 ppm de NO_2 , alors que la détérioration la plus importante est constatée à 13 ppm de SO_2 et 5 ppm de NO_2 (cf. V 81, tableau 2) ;
- avec le taux d'humidité ; il est nécessaire d'avoir au moins 80 %, mais les effets les plus grands sont obtenus à partir de 90 % d'humidité relative ;
- avec le temps d'exposition.

Effet de SO_2 + NO_2 suivi d'un traitement complémentaire

Les résultats sont rassemblés dans le tableau 2. Le nombre d'expériences étant restreint, nous devons être prudents dans nos conclusions. Cependant, en comparant V 105 et V 109 (tableau 2) à V 111 (tableau 1) ainsi que V 97 (tableau 2) à V 96 (tableau 1),

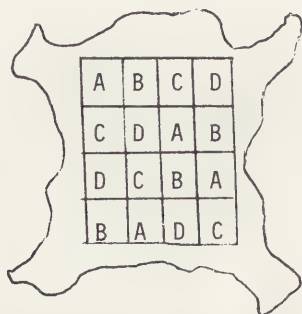
il apparaît que les U.V. accélèrent la détérioration, car le taux de composés azotés solubles est légèrement augmenté*.

D'autre part, un traitement à forte humidité n'augmente pas la détérioration : V 87 (tableau 2) est équivalent à V 86 (tableau 1).

Signalons le cas particulier du traitement V 81 où la détérioration est de loin la plus importante ; cet effet est probablement dû à une forte concentration en polluants, conjuguée à un taux d'humidité élevé.

Effet in-situ

Parallèlement à l'étude en laboratoire, des échantillons de cuir et de parchemin sont exposés à Rouen** dans quatre sites différents : la Bibliothèque municipale, la tour des Archives, la Faculté des Sciences et la Mairie de Maromme. Les peaux ont été découpées de la manière suivante :



A = témoin

B = temps 1

C = temps 2

D = temps 3

(3 temps d'exposition différents)

Les parties B, C et D d'un cuir de veau, de chèvre, de mouton et d'un parchemin sont suspendues dans chacun de ces sites.

Les éprouvettes seront analysées (analyse mécanique et chimique) à des intervalles de temps qui seront déterminés grâce à des tests effectués sur de petits fragments adjoints pour sondage (10 au total). Jusqu'à présent, nous en avons analysé trois séries : après 6 mois, un an et 18 mois d'exposition. La taille de ces pièces ne nous a pas permis de doubler les analyses, aussi nous bornerons-nous à faire uniquement des constatations générales sur les premiers résultats obtenus :

* Des essais antérieurs, dans les mêmes conditions de température et d'humidité, ont montré que les UV ne modifient pas la composition chimique du cuir.

** Nous tenons à remercier ici Monsieur BOULLARD, Professeur à la Faculté des Sciences de Rouen, pour l'aide qu'il nous a apportée dans la réalisation de ce travail.

- *Pour les cuirs*, les pH diminuent (de 0,5 à 1 unité pH). Nous avons observé un phénomène inverse sur les cuirs disposés à Maromme dont le pH augmente de 1 unité en même temps que l'indice de différence diminue : ceci peut suggérer une fixation d'ammoniaque, d'autant que la première fraction du dosage des composés azotés solubles augmente de façon sensible. Ce phénomène inhabituel peut cependant s'expliquer, dans le cas présent, par le fait qu'une fabrique d'engrais est implantée dans la région.

Les taux de sulfates solubles augmentent et pour quelques-uns, dans des proportions assez considérables.

Les taux de composés azotés solubles sont assez peu modifiés, à l'exception de ce qui a été constaté dans les cuirs de Maromme.

- *Pour les parchemins*, les pH diminuent légèrement. Dans l'ensemble, on constate une augmentation du taux des sulfates solubles ; de plus, certains d'entre eux accusent une hydrolyse assez poussée qui se traduit par une élévation importante du taux des composés azotés solubles.

En fonction de tous ces résultats, nous pensons judicieux de faire notre premier prélèvement d'échantillons après deux ans d'exposition.

L'anhydride sulfureux, polluant fréquemment émis par les atmosphères urbaines et industrielles, est un des principaux responsables de la détérioration des cuirs ; mais il n'est agressif que sous sa forme oxydée.

Dans nos expériences, nous avons constaté que la vitesse d'oxydation est lente, même en présence de catalyseurs et à forte humidité, sans l'action simultanée d'un oxydant ; le peroxyde d'azote, qui est également toujours présent dans les atmosphères polluées, a été utilisé dans ce but. Les effets constatés sur les cuirs, bien que devant être encore accentués, devraient nous permettre d'aborder la deuxième phase de notre travail, la protection des reliures.

D'autre part, l'exposition à Rouen nous a permis de mettre en évidence les premiers signes de détérioration dans des temps assez courts. Nous pensons que ces résultats "prometteurs" aboutiront à une corrélation entre les phénomènes constatés in-situ et ceux reproduits expérimentalement.

REFERENCES BIBLIOGRAPHIQUES

- (1) BEEBE (C.W.), FREY (R.W.), HANNIGAN (M.V.), *A comparison of gas chamber tests of bookbinding leather with a long time atmospheric exposure*, J. of the American Leather Chemists Assoc., 1956, 51, p. 20-31
- (2) BENARIE (M.), MENARD (T.) et NONAT (A.), *Etude de la transformation de l'anhydride sulfureux en acide sulfurique en relation avec les données climatologiques, dans un ensemble urbain à caractère industriel*, Rouen, Atmos. Environ., 1973, 7, p. 403 21

- (3) COX (R.A.) and PENKETT (S.A.), *Oxidation of atmospheric SO₂ by products of the ozone-olefin reaction*, *Nature*, 1971, 230, p. 321-2
- (4) COX (R.A.) and PENKETT (S.A.), *Photo-oxidation of atmospheric SO₂*, *Nature*, 1971, 229, p. 486-8
- (5) FIAUD (C.), *Progrès récents dans l'évaluation de la tenue à la corrosion de l'or et de l'argent*, *Surfaces*, 127, juin 1979, p. 35-7
- (6) FREIBER (J.), *Effect of relative humidity and temperature on iron-catalyzed oxidation of SO₂ in atmospheric aerosols*, *Environ. Sci. and Technology*, 1974, 8, p. 731-4
- (7) FREY (R.W.), BEEBE (C.W.), *A proposed standard gas chamber for accelerated ageing of leather*, *J. of the American Leather Chemists Assoc.*, 1940, 35, p. 180-92
- (8) INNES (R.F.), *The Preservation of vegetable tanned leather against deterioration*, *Progress in leather science 1920-1945*, London : B.L.M.R.A., 1948, p. 426-50
- (9) JUNGE (C.E.) and RYAN (T.G.), *Study of the SO₂ oxidation in solution and its rôle in atmospheric chemistry*, *Quart. Journal of the Royal Meteorological Society*, 1958, 84, p. 46-55
- (10) KATZ (M.), *Analysis of inorganic gaseous pollutants*, *Air Pollution*, Ed. A.C. Stern, 2nd Ed., New-York, London : Academic Press, 1968, vol. II, p. 58-60
- (11) KATZ (M.), *op. cit.*, p. 80-83
- (12) STOPPERKA (K.), WOLF (F.), SUESS (G.), *Gas-phase reaction of nitrogen dioxide and sulfur dioxide*, *Z. Anorg. Allg. Chem.*, 1968, 359 (1-2), p. 14-29 (en allemand).

TABLEAU N° 1

EFFET DE SO_2 + NO_2 sur le cuir

	T *	pH	Ind. diff.	Mat. solu- bles%	Sulf. solu- bles%	Azote soluble %			Tr	Traitement
						amm.	proté- ique	total		
V 67	1	3,25	1	1,9	0,48	0,01	0,03	0,04		2 sem. 25°C 95 % HR 7 + 2 ppm
V 76	1	3,00	0,90		0,45	0,02	0,02	0,04		3 sem. 25°C 95 % HR 7 + 2 ppm
V 77	1	3,20	1	1,9	0,44	0,01	0,03	0,04		4 sem. 25°C 95 % HR 7 + 2 ppm
V 86	2	2,80	1	2,3	0,50	0,01	0,04	0,05		4 sem. 30°C 75 % HR 9 + 3 ppm
V107	3	2,65	1	2,3	0,82	0,02	0,03	0,05	81°C	4 sem. 30°C 90 % HR 9 + 3 ppm
V111	3	2,30	1	3,3	1,46	0,06	0,04	0,10	76°C	4 sem. 30°C 95 % HR 12 + 4 ppm
V 96	2	2,60	0,95	2,2	0,79	0,06	0,03	0,09	80°C	4 sem. 30°C 85 à 95 % HR 2 sem. 9 + 3 ppm 2 sem. 13 + 5 ppm
V 80	1	2,15	0,95	3,3	1,74	0,04	0,04	0,08		4 sem. 30°C 90 % HR 9 + 3 ppm
V 98	2	2,35	0,95	3,9	1,62	0,08	0,06	0,14		6 sem. 30°C 90 % HR 9 + 3 ppm
V 90	2	2,70	1	3,6	1,20	0,02	0,06	0,08		7 sem. 30°C 70 à 85 % HR 11 + 3 ppm
V100	2	2,25	1	3,3	1,86	0,09	0,08	0,17	73°C	9 sem. 30°C 90 % HR 9 + 3 ppm
V 94	2	2,35	0,95	3,4	1,87	0,09	0,08	0,17		12 sem. 30°C 90 % HR 9 + 3 ppm

* Témoins

1	4,10	0,60	2,1	0,19	0	0,03	0,03		V 67, V 76, V 77, V 80
2	4,75	0,65	2,0	0,19	0	0,03	0,03	82°C	V 86, V 96, V 98, V 92, V 100, V 94
3	4,15	0,65	2,2	0,24	0	0,03	0,03	82°C	V 107, V 111

TABLEAU N° 2

EFFET DE SO_2 + NO_2 sur le cuir
suivi d'un traitement aux U.V. ou à l'humidité

U.V.	T *	pH	Ind. diff.	Mat. solu- bles%	Sulf. solu- bles%	Azote soluble %			Tr	Traitement
						amm.	proté- ique	total		
V 105	3	2,70	1	3,1	1,08	0,10	0,08	0,18	80°C	3 sem. 30°C 95 % HR 9 + 3 ppm/+ 2 sem. UV
V 109	3	2,60	0,85	3	1,16	0,09	0,07	0,16		3 sem. 30°C 95 % HR 9 + 3 ppm/+ 2 sem. UV
V 92	2	2,85	1	2,3	0,96	0,10	0,07	0,17	80°C	3 sem. 30°C 85 à 95 % HR 9 + 3 ppm/+ 2 sem. UV
V 97	2	2,55	0,95	2,8	0,79	0,08	0,08	0,16		4 sem. 30°C 85 à 95 % HR 9 + 3 ppm/+ 2 sem. UV

Humidité
30°C 95 % HR

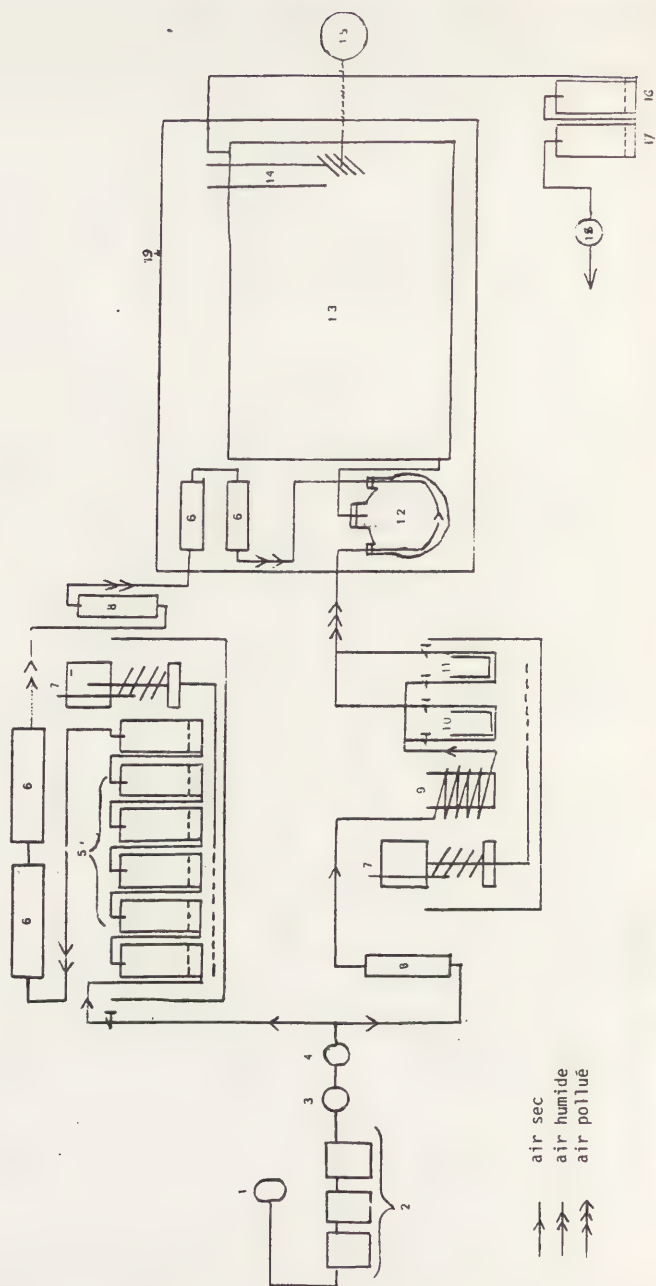
V 88	2	2,90	1	2,7	0,89	0,04	0,03	0,07	80°C	4 sem. 30°C 75 % HR 9 + 3 ppm/+ 3 sem. étuve
V 81	2	2,20	0,90	4,8	3,04	0,16	0,24	0,40	76°C	5 sem. 30°C 85 à 95 % HR 13 + 5 ppm/+ 4 sem. étuve

Humidité
+ UV

V 93	2	3	1	2,2	0,72	0,07	0,07	0,14	78°C	3 sem. 30°C 85 à 95 % HR 9 + 3 ppm/+ 2 sem. étuve + 1 sem. UV
------	---	---	---	-----	------	------	------	------	------	---

* Témoins 2 et 3 : voir tableau n° 1

- 1) Arrivée d'air comprimé
- 2) Batterie de filtres à air
 - a) dépoussiéreur
 - b) déshuileur
 - c) tamis moléculaires
- 3) Manodétendeur basse pression. 0 à 1 bar
- 4) Régulateur de pression
- 5) Batterie de 6 flacons servant à humidifier l'air
- 6) Condenseurs
- 7) Régulateurs de température de 10 à 50°C avec précision $\pm 0,01$
- 8) Débitmètres de 0 à 150 l/h
- 9) Serpentin servant à conditionner l'air
- 10)
- 11) Tubes en U pouvant recevoir un tube de perméation
- 12) Flacon mélangeur
- 13) Chambre d'exposition des échantillons en plexiglas
- 14) Mesure de température et d'humidité
- 15) Système de brassage de l'air
- 16) H_2O_2 arrétant l'acidité résiduelle
- 17) Piège à eau
- 18) Compteur de débit
- 19) Etuve thermostatée.

SCHEMA DU MONTAGE POUR L'ETUDE DE L'EFFET DU SO_2 SUR LE CUIR

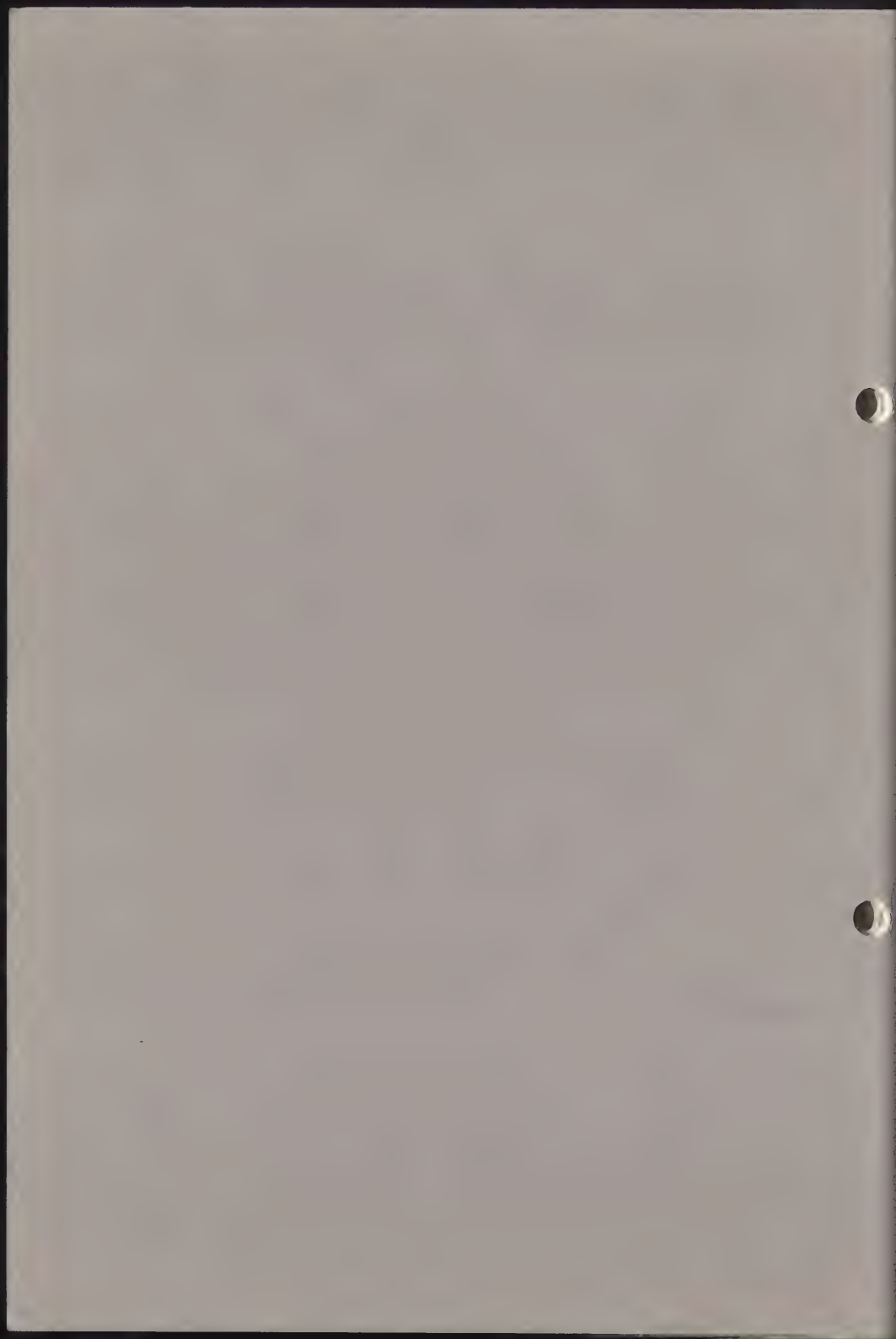
81/14/7

CONSOLIDATION DE LA COUCHE PICTURALE DES
ENLUMINURES AVEC POLYMERES SYNTHETIQUES PURS

Mariagrazia Zappalà Plossi et Paolo Crisostomi

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Documents graphiques et
photographiques



CONSOLIDATION DE LA COUCHE PICTURALE DES ENLUMINURES AVEC POLYMERES SYNTHETIQUES PURS

Mariagrazia Zappalà Plossi et Paolo Crisostomi

Mariagrazia Zappalà Plossi
Laboratorio di Chimica
Istituto Centrale per la Patologia del Libro
Via Milano 76
00184 Roma
Italie

Paolo Crisostomi
Scuola per la Conservazione e il Restauro
Istituto Centrale per la Patologia del Libro
Via Milano 76
00184 Roma
Italie

RESUME

Dans le cadre d'une recherche sur le fixage de la couche picturale des enluminures sur parchemin, on a expérimenté cinq types de polymères synthétiques purs. On a effectué des essais sur des échantillons de parchemin peint pour observer l'effet pratique des polymères purs en étude. Le solvant utilisé influence le degré de pénétration du polymère. Le meilleur effet esthétique est obtenu avec la méthylcellulose dissoute dans le chlorure de méthylène/méthanol.

L'acétate de cellulose par contre donne un résultat tout-à-fait négatif en formant une couche blanchâtre sans aucune pénétration.

On a effectué aussi des mesures de flexibilité sur parchemin non-traité, et traité avec les polymères choisis.

INTRODUCTION

On rencontre souvent dans les manuscrits des enluminures présentant un mauvais état de conservation : celui-ci est dû non seulement à une altération chromatique des pigments, mais surtout à leur soulèvement du support de parchemin spécialement dans les parties exposées aux mouvements mécaniques.

Les causes de dégradation sont diverses; en général on observe un vieillissement de tous les éléments de l'enluminure et surtout des liants utilisés pour faire adhérer le pigment au support.

Dans certains cas il est donc nécessaire de procéder à un fixage de la couche picturale, en lui donnant, dans la mesure du possible, élasticité et résistance.

On peut choisir soit des matériaux déjà utilisés à l'époque, comme la colle de parchemin, la gomme arabique, etc... (1,2,3), soit des produits modernes synthétiques (3,4,5,6,7,8). Dans ce cas il est indispensable que le produit permette une bonne réversibilité (3,4,8) aussi après vieillissement.

Pour le traitement des parchemins enluminés il est nécessaire que le produit synthétique utilisé soit soluble aux solvants organiques; en effet l'eau employée comme telle peut causer des dommages et surtout dissoudre les anciens liants dans lesquels sont mélangés les pigments.

Actuellement on cherche une résine possédant certaines caractéristiques bien précises : élasticité et résistance aux agents biologiques pour éviter l'adjonction de plastifiants (8,9) et fongicides. Pour ces raisons on a limité notre étude aux produits chimiquement purs.

Les produits choisis sont :

- Ethylcellulose
- Méthylcellulose
- Acétate de polyvinyle
- Acétate de cellulose
- Polyméthylméthacrylate

Tous les polymères en étude sont des produits de la B.D.H. Chemicals Ltd., Poole, England.

CARACTERISTIQUES DES POLYMERES CHOISIS

Ethylcellulose

L'éthylcellulose est obtenue par l'action du chlorure d'éthyle sur l'alcali cellulose en autoclave (10).

L'éthylcellulose complètement éthérifiée, c'est-à-dire avec un degré de substitution 3 (correspondant à un contenu de groupes éthoxydes de 54.88%) a les caractéristiques suivantes : peu soluble, non thermo-plastique, peu flexible, peu tenace. Elle ne présente donc guère d'applications pratiques (10,11,12).

Selon le contenu de groupes éthoxydes on obtient des éthylcelluloses à propriétés diverses : elles sont solubles à l'eau seulement lorsque le degré d'éthérification est peu élevé; un contenu majeur en éthoxydes augmente la solubilité dans les solvants organiques jusqu'à un "optimum" qui correspond à 47.5 ÷ 49%. L'acétate d'éthyle et le chlo-

rure d'éthylène sont de bons solvants pour tous les types d'éthylcelluloses (10,11,12).

Le produit pur utilisé dans notre recherche est une poudre blanche qui possède un degré de substitution de $2.42 \div 2.53$ correspondant à un contenu d'éthoxyles de $47.5 \div 49\%$; la viscosité d'une solution à 5% w/w dans le toluène/éthanol 80:20 à 25°C. est d'environ 14 cP (15).

Méthylcellulose

Les méthylcelluloses (10,11,12) sont des poudres blanchâtres, inodores, sans saveur, non toxiques, qui gonflent dans l'eau en formant des solutions colloïdales visqueuses.

Elles sont obtenues industriellement à partir de l'alcali cellulose (10) par réaction avec le chlorure de méthyle en autoclave.

En général les méthylcelluloses sont solubles dans l'eau chaude; en outre leur solubilité dépend du degré de substitution, c'est-à-dire du nombre moyen des groupes méthoxyliés liés à une molécule de glucose.

Les méthylcelluloses (11) peu substituées (avec un teneur en méthoxyliés de $6\% \div 18\%$) sont peu solubles à l'eau mais très solubles dans les solutions alcalines.

Les méthylcelluloses fortement substituées (avec un teneur en méthoxyliés de $48 \div 32\%$) sont solubles dans l'eau froide; avec la hausse de température la solution floccule. Les méthylcelluloses qui contiennent environ le 30% de méthoxyliés sont solubles dans les solvants organiques.

Le produit pur utilisé dans notre recherche est une poudre blanche qui possède un degré moyen de substitution de 1.9 qui correspond à environ 30% de méthoxyliés. La solution à 1.5% w/w dans le chlorure de méthylène/méthanol 80:20 possède une viscosité (selon le Viscosimètre de Ostwald) à 20°C de 500 à 600 cP (15).

Acétate de Polyvinyle

L'acétate de polyvinyle (10) est obtenu par la polymérisation de l'acétate de vinylyle en présence de peroxydes, persulfates etc... La polymérisation peut être effectuée en solution, en émulsion ou en suspension.

Les propriétés des produits solides dépendent du degré de polymérisation. L'acétate de polyvinyle commercial a un poids moléculaire qui varie entre 5000 et 20 000. A poids moléculaire faible on obtient des produits mous, à poids moléculaire plus élevé on obtient des pro-

duits solides, thermoplastiques, incolores, inodores, sans saveur et non toxiques.

L'acétate de polyvinyle est insoluble dans l'eau et dans les alcools supérieurs anhydres. Il est soluble dans les cétones, les hydrocarbures aromatiques, les solvants chlorurés, l'alcool méthylique et l'alcool éthylique à 95%.

Commercialisé sous forme de film, c'est un des polymère les plus utilisé; en outre l'acétate de polyvinyle est un élément de base dans la composition d'un grand nombre de colles et d'adhésifs.

Le produit pur qui a été utilisé pour notre recherche possède un poids moléculaire de 45000 (15). et un degré d'amollissement à 106°C : la viscosité d'une solution à 8.6% w/w dans le benzène à 20°C est de $6 \div 8$ cP.

Acétate de cellulose

L'acétate de cellulose (10,11,12) est obtenu par acétylation de la cellulose avec l'anhydride acétique en présence d'un catalyseur déshydratant (acide sulfurique, chlorure de zinc, etc.). Il résulte de cette manière une cellulose complètement acétylée (trois groupes acétiques par unité de glucose), soluble dans le chloroforme et insoluble dans l'acétone et dans d'autres solvants.

Les acétates de cellulose à degré d'acétylation plus faible sont préparés par hydrolyse partielle du triacétate en obtenant des produits solubles et stables. Par ex. le 2.5 acétate (52% d'acide acétique) est soluble dans l'acétone et dans d'autres solvants; le diacétate est soluble dans l'alcool chaud et dans des mélanges d'hydrocarbures et alcools, de cétones inférieures etc.

Tous les acétates (11) sont très solubles dans l'acide acétique glacial, dans l'acide formique et dans un mélange de chlorure de méthylène/méthanol 9 : 1.

On peut obtenir les acétates de cellulose sous forme de flocons, de poudre blanche inodore et sans saveur, en film ou en feuilles transparentes, translucides ou opaques.

L'acétate de cellulose utilisé dans notre recherche est une poudre blanche contenant de 52% à 53.5% d'acide acétique : la viscosité d'une solution à 6% dans un mélange d'acétone/eau à 95% à 25°C, est de $70 \div 110$ cP. (Viscosimètre No. 3 BSS).

Polyméthacrylate de méthyle

Le polyméthacrylate (10,11,14) est le produit le plus important du groupe des polyméthacrylates alcalins. C'est un polymère thermoplastique qui possède une transparence, une limpidité et une brillance excellentes; il présente une bonne résistance à la lumière, au vieillissement, aux acides dilués, aux bases diluées et concentrées, aux agents atmosphériques.

Il est obtenu industriellement par polymérisation en bloc, en suspension, en émulsion ou en solution selon l'usage requis, (plaques, feuilles, laques, vernis etc.). Il est soluble dans les hydrocarbures chlorurés, dans les hydrocarbures aromatiques, dans les alcools aldéhydes et les cétones.

Le polymère choisi pour notre recherche se présente sous forme de perles très petites ayant un point de fusion à 225°C : la viscosité (avec un gradient de vitesse de 1120 sec.^{-1}) à 240°C , est de 2.80 KiloPoise (15).

APPLICATION DES POLYMERES

D'après des indications bibliographiques (8,10,11), on a effectué des essais de solubilité parmi les polymères cités pour obtenir des solutions limpides.

Par la suite des essais préliminaires ont été effectués afin de choisir pour chaque polymère une concentration optimale qui maintienne les conditions de limpidité et qui permette une bonne cohésion et adhérence au support.

Les concentrations choisies sont :

- Ethylcellulose à 5% dans le toluène/éthanol 80 : 20
- Méthylcellulose, haute substitution, à 0.5% dans le chlorure de méthylène/méthanol 80 : 20
- Acétate de polyvinyle à 10% dans le benzène
- Acétate de polyvinyle à 10% dans l'alcool éthylique
- Acétate de cellulose à 3% dans l'acétone/eau 95 : 5
- Polyméthylméthacrylate à 10% dans le dichloréthane
- Polyméthylméthacrylate à 4% dans l'acétone

On a procédé à une évaluation qualitative d'adhérence et de cohésion en mélangeant du cinabre avec les solutions des polymères et en les étendant à l'aide d'un pinceau sur du parchemin (agneau de fabrication artisanale de la Maison Gentili). Pour chaque cas on a remarqué une assez bonne adhérence du pigment au support de parchemin. Il est intéressant de noter que pour chaque résine on a obtenu des graduations différentes de couleur du cinabre; ex. : la couleur devient beaucoup plus claire

avec l'acétate de cellulose.

Malgré l'impression en noir et blanc, on distingue les différentes tonalités sur la photo N° 1.

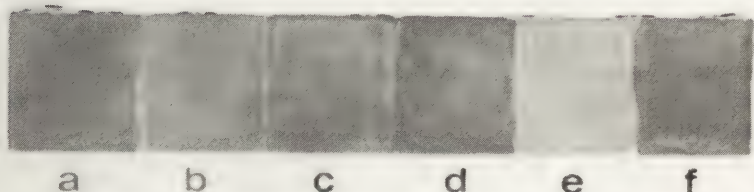


Fig. 1

Mélange du cinabre avec les polymères synthétiques :

- a) éthylcellulose 5% (toluène/éthanol)
- b) méthylcellulose 0.5% (chlorure de méthylène/méthanol)
- c) acétate de polyvinyle 10% (benzène)
- d) acétate de polyvinyle 10% (alcool éthylique)
- e) acétate de cellulose 3% (acétone/eau)
- f) polyméthylméthacrylate 10% (dichloréthane)

Pour évaluer l'effet esthétique, c'est-à-dire la brillance, le changement de couleur et la patine superficielle, les polymères mentionnés ont été appliqués au pinceau sur une couche picturale. Dans ce but on a recouvert une planche de bois avec du parchemin légèrement humidifié et fixé avec des clous après tirage. Le parchemin une fois sec a été subdivisé en deux parties : sur la partie inférieure on a étendu une couche de bleu outremer, sur la partie supérieure une couche de cinabre. Ces deux pigments ont été liés avec une solution de gomme arabique à 10%. On a choisi la gomme arabique qui est un des "medium" les plus employés dans l'exécution des enluminures anciennes; de plus elle permet d'obtenir des échantillons homogènes.

L'aspect esthétique final est reporté sur le tableau N° 1, ainsi que sur la photo 2. Le changement chromatique se remarque davantage sur une couleur sombre. Esthétiquement,

quement la méthylcellulose à haute substitution dissoute dans le chlorure de méthylène/méthanol, donne de meilleurs résultats. L'acétate de cellulose est négatif, formant une couche blanchâtre sans aucune pénétration.

MESURES DE FLEXIBILITE DU PARCHEMIN TRAITE

Les variations de flexibilité du parchemin traité avec les solutions des résines en étude ont été exécutées à l'aide d'un flexomètre de la Maison Enrico Toniolo S.A.S Milano.

L'échantillon de parchemin (1.5 x 9.5 cm) est tenu une extrémité par un étau fixe, l'autre extrémité est appuyée contre une roulette; en manoeuvrement le curseur, l'échantillon se plie à 90° et subit un moment de flexion. En considérant -constante- la longueur de flexion on peut exprimer le résultat en gramme comme force de flexion : à une valeur élevée correspond une flexibilité moindre.

Tous les échantillons ont été coupés dans le sens "tête-queue" de l'animal, en utilisant la partie dorsale de la peau. Les mesures de flexibilité ont été effectuées en fixant le côté "tête" de l'échantillon dans l'étau. On a fait une 1ère série de mesures côté "fleur" interne de l'échantillon, et une seconde série de mesures côté "chair" interne. Pour compenser l'hétérogénéité du parchemin, pour chaque échantillon on a procédé de la manière suivante :

- mesures de flexibilité avant traitement
- " " " après traitement seulement
- " " " avec le solvant du polymère
- " " " après traitement avec le polymère dissout dans les solvants cités précédemment.

Les mesures relatives aux traitements effectués soit en immersion soit au pinceau, sont regroupées sur le tableau 2 et 3.

Les mesures obtenues ont donc une valeur purement indicative, cependant on peut y trouver des éléments intéressants : bon nombre de solvants augmentent la flexibilité du parchemin; l'éthylcellulose offre une bonne flexibilité.

Etant donné le sujet de la recherche, cette étude n'approfondit pas les réactions dues aux différents solvants; il serait intéressant par la suite d'analyser l'effet des solvants à long terme car l'augmentation de flexibilité pourrait être fictive, et après un certain laps

de temps le parchemin pourrait recouvrer sa flexibilité initiale.

CONCLUSION

Les problèmes concernant le fixage des enluminures sont innombrables, ce travail n'en reflète qu'un des aspects et traite plus particulièrement des questions pratiques.

Le meilleur résultat esthétique est obtenu avec la méthylcellulose à haute substitution dissoute dans le chlorure de méthylène/méthanol; il dépend aussi du solvant utilisé pour dissoudre le polymère en agissant probablement sur sa pénétration.

Indépendamment des résultats obtenus, les auteurs sont en principe contraires à l'usage du fixage qui devrait être limité aux cas particulièrement graves de dégradation.

Les auteurs remercient particulièrement Mlle Isabell Anex, élève à l'Ecole de Conservation et Restauration de l'Istituto Centrale per la Patologia del Libro, pour son aide efficace dans la traduction française.

Tableau 1

Produit	changement de couleur		brillance	patine superficielle
	sur cinabre	sur bleu outremer		
Ethylcellulose 5% (toluène/éthanol)	+	++	0	+
Méthylcellulose 0.5% (chlorure de méthylène/ méthanol)	0	+	0	+
Acétate de polyvinyle 10% (benzène)	++	++	++	++
Acétate de polyvinyle 10% (alcool éthylique)	++	++	++	++
Acétate de cellulose 3% (acétone/eau)	+++	+++	+++	+++
Polyméthylméthacrylate 10% (dichlorétane)	++	++	++	++
Polyméthylméthacrylate 4% (acétone)	++	++	++	++

0 = nul
+ = faible
++ = moyen
+++ = fort

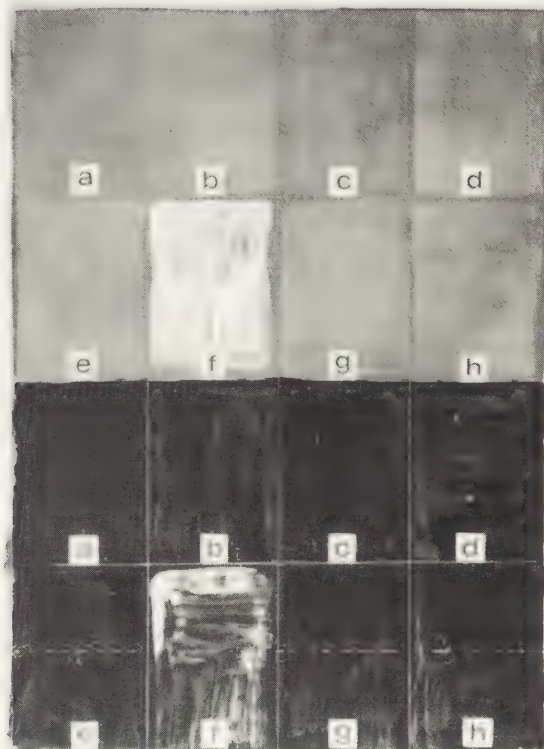


Fig. 2 Effet esthétique sur cinabre et bleu outremer des polymères suivants:

- a) non traité
- b) éthylcellulose 5% (toluène/éthanol)
- c) méthylcellulose 0.5% (chlorure de méthylène/méthanol)
- d) acétate de polyvinyle 10% (benzène)
- e) acétate de polyvinyle 10% (alcool éthylique)
- f) acétate de cellulose 3% (acétone/eau)
- g) polyméthylméthacrylate 4% (acétone)
- h) polyméthylméthacrylate 10% (dichloréthane)

Mesures de flexibilité de parchemin traité par immersion avec les polymères choisis
(a)

produit	côté fleur interne		côté chair interne	
	n.t.	traité avec le solvant	n.t.	traité avec le solvant polym+ solvant
Etc.	3.87	3.68	6.60	6.10 3.25
Etc.	1.38	1.20	2.15	1.70 2.20
Etc.	3.80	2.87	5.23	4.60 5.60
Met. c.	2.60	2.10	4.55	3.90 4.45
Met. c.	1.40	1.00	2.50	2.20 2.90
Met. c.	2.89	1.90	6.00	5.19 4.20
Ac. P. b.	1.85	1.90	2.59	2.65 2.90
Ac. P. b.	3.80	3.85	5.30	5.40 5.90
Ac. P. b.	4.30	4.50	5.56	5.64 5.50
Ac. P. e.	2.32	0.80	4.40	4.02 3.72
Ac. P. e.	3.30	1.39	4.00	3.80 2.70
Ac. P. e.	2.50	1.60	5.15	4.58 4.38
Ac. Cl.	0.83	--	1.78	1.60 --
Ac. Cl.	1.40	0.58	2.15	2.08 2.10

%

Suite du tableau précédent

Ac. Cl.	3.23	2.60	--	5.50	4.70	--
P.m.m.a.	1.23	0.93	1.42	2.70	2.50	3.20
P.m.m.a.	2.08	1.90	1.65	3.65	3.50	4.40
P.m.m.a.	4.70	4.40	4.40	5.10	5.00	6.80
P.m.m.d.	1.98	1.98	2.30	2.70	2.70	3.20
P.m.m.d.	2.12	2.12	2.21	3.70	3.70	4.10
P.m.m.d.	3.98	3.98	4.27	5.90	5.90	--

n.t. = non traité

Etc. = éthylcellulose à 5% dans le toluène/éthanol 80:20

Met. c. = méthylcellulose à 0.5% dans le chlorure de méthylène/méthanol 80:20

Ac. P. b. = acétate de polivinyle à 10% dans le benzène

Ac. P. e. = " " " à 10% dans l'alcool éthylique

Ac. Cl. = acétate de cellulose à 3% dans l'acétone/eau 95:5

P.m.m.d. = polyméthylméthacrylate à 10% dans le dichloréthane

P.m.m.a. = " " " à 4% dans l'acétone

(a) On a effectué mesure sur trois échantillons pour chaque polymère.

Tableau 3

Mesures de flexibilité de parchemin traité au pinceau avec les polymères choisis (a)

produit	côté fleur interne		côté chair interne			
	n.t.	traité avec le solvant	traité avec polym+solvant	n.t.	traité avec le solvant	traité avec polym+solvant
Etc.	1.90	1.45	1.50	3.70	4.10	3.30
Etc.	1.60	1.60	1.48	4.00	3.78	3.15
Etc.	2.80	1.68	1.76	4.60	4.82	4.43
Met. c.	1.90	1.70	2.10	3.70	3.68	4.58
Met. c.	2.40	1.82	2.60	4.02	4.40	4.78
Met. c.	0.95	--	1.30	3.95	4.22	4.32
Ac. P. b.	1.20	0.95	1.13	4.21	4.22	4.28
Ac. P. b.	1.60	1.50	1.75	4.00	3.90	4.61
Ac. P. b.	1.42	1.38	1.30	3.85	3.90	4.53
Ac. P. e.	2.20	1.64	2.35	4.20	4.04	4.67
Ac. P. e.	1.65	--	1.80	4.70	3.43	5.40
Ac. P. e.	1.90	--	2.20	3.65	4.58	4.55
Ac. Cl.	2.53	1.78	3.22	4.40	4.23	5.80
Ac. Cl.	1.70	0.98	1.97	3.52	4.61	4.37
						%

%

Suite du tableau précédent

Ac. Cl.	2.30	1.93	2.73	4.30	3.59	5.25
P.m.m.a.	1.90	0.92	2.39	4.08	4.28	4.59
P.m.m.a.	2.20	1.73	2.58	4.38	4.20	4.64
P.m.m.a.	2.28	1.92	2.76	4.92	4.80	5.63
P.m.m.d.	2.50	2.33	2.22	4.53	4.47	5.10
P.m.m.d.	3.00	2.95	3.38	4.35	4.50	5.38
P.m.m.d.	2.20	2.20	1.90	4.20	4.60	4.98

n.t. = non traité

Etc. = éthylcellulose à 5% dans le toluène/éthanol 80:20

Met. c. = méthylcellulose à 0.5% dans le chlorure de méthylène/méthanol 80:20

Ac. P. b. = acétate de polivinyle à 10% dans le benzène

Ac.P. e. = " " à 10% dans l'alcool éthylique

Ac. Cl. = acétate de cellulose à 3% dans l'acétone/eau 95:5

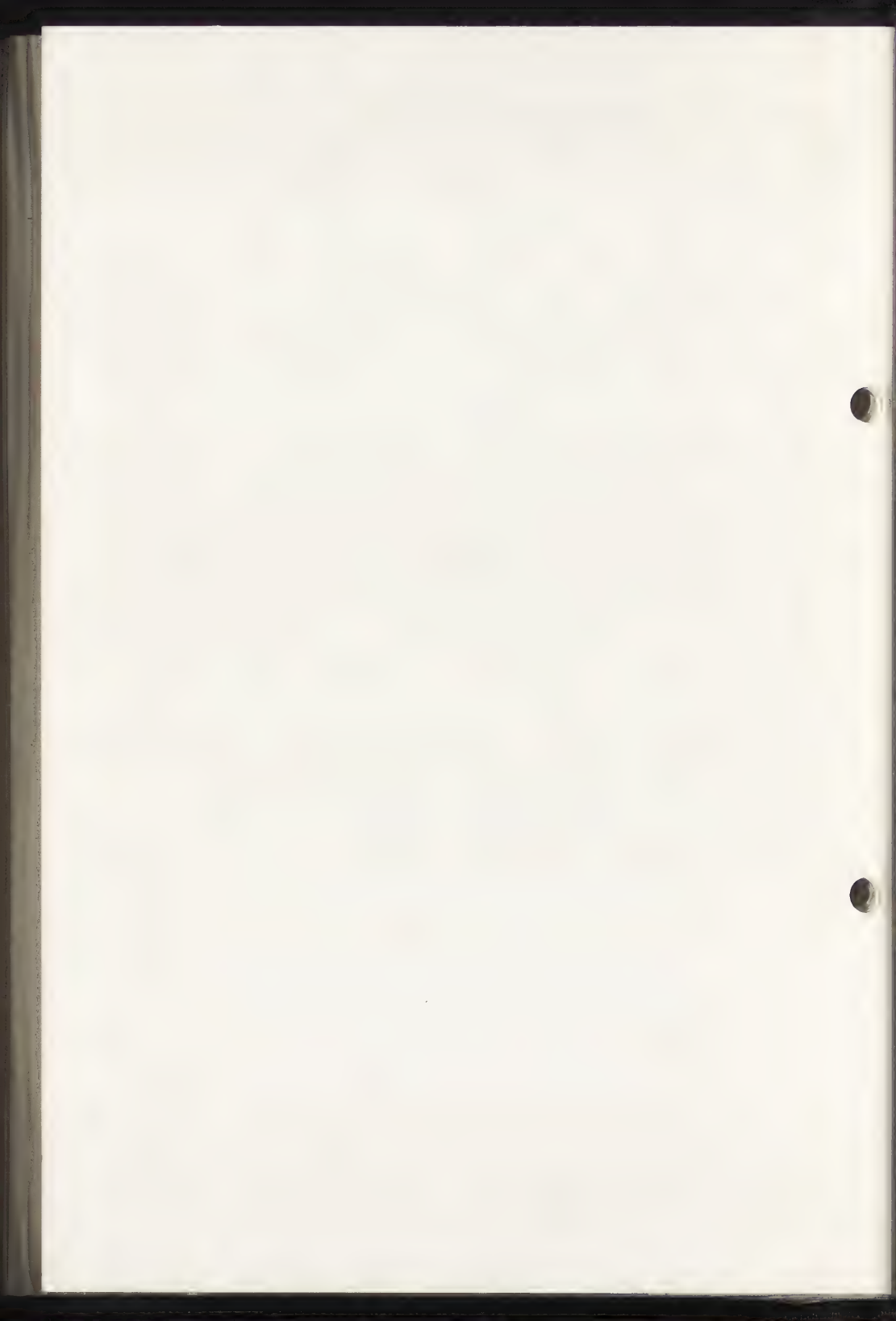
P.m.m.d. = polyméthylméthacrylate à 10% dans le dichloréthane

P.m.m.a. = " " à 4% dans l'acétone

(a) On a effectué mesure sur trois échantillons pour chaque polymère.

BIBLIOGRAPHIE

- 1) G. STRINI, Boll. I.P.L., XVI, I-11, 44-51, 1957.
- 2) F. FLIEDER, Studies in Conservation, 13, n°2, 49, 1968.
- 3) V. RADOSAVLJEVIC, Conservation of Miniatures, ICOM, Madrid, 2-8 oct. 1972.
- 4) A. BALLESTREM, E. DE WITTE, Le problème de la consolidation des couches picturales des enluminures/ Quelques essais, ICOM, Madrid, 2-8 oct. 1972.
- 5) J. PORCHER, Rapport sur le traitement des manuscrits à peinture, ICOM, Barcelone, octobre 1961.
- 6) G.Z. BYKOVA, A.V. IVANOVA, I.P. MUKRETZOVA, Conservation Methods for Medieval Miniatures on Parchment, ICOM, Madrid, 2-8 oct. 1972.
- 7) B. MARCONI, Studies in Conservation, 7, n°1, 17, 1962.
- 8) Matières synthétiques employées pour la conservation des biens culturels, "La préservation des Biens Culturels", Paris, UNESCO, 1969.
- 9) M. ZAPPALA' PLOSSI, Boll. I.C.P.L. XXXIV, 35, 1976-77.
- 10) V. VILLAVECCHIA, G. EIGENMANN, "Nuovo Dizionario di Merceologia e Chimica Applicata", U. Hoepli éd., Milano, 1975.
- 11) HUMMEL/SCHOLL, "Infrared Analysis of Polymers, Resins and Additives, An Atlas", Vol. I, Part 1: Text, Wiley-Interscience, New York, 1971.
- 12) W.D. PAIST, "Manuali delle Materie Plastiche /Derivati Cellulosici", Aldo Martello éd., Milano, 1963.
- 13) W. MAYO SMITH, "Manuali delle Materie Plastiche/ Resine Viniliche", Aldo Martello éd., Milano, 1962.
- 14) M.B. HORN, "Manuali delle Materie Plastiche/Resine Acriliche", Aldo Martello éd., Milano, 1963.
- 15) Indications de la Maison de Production.



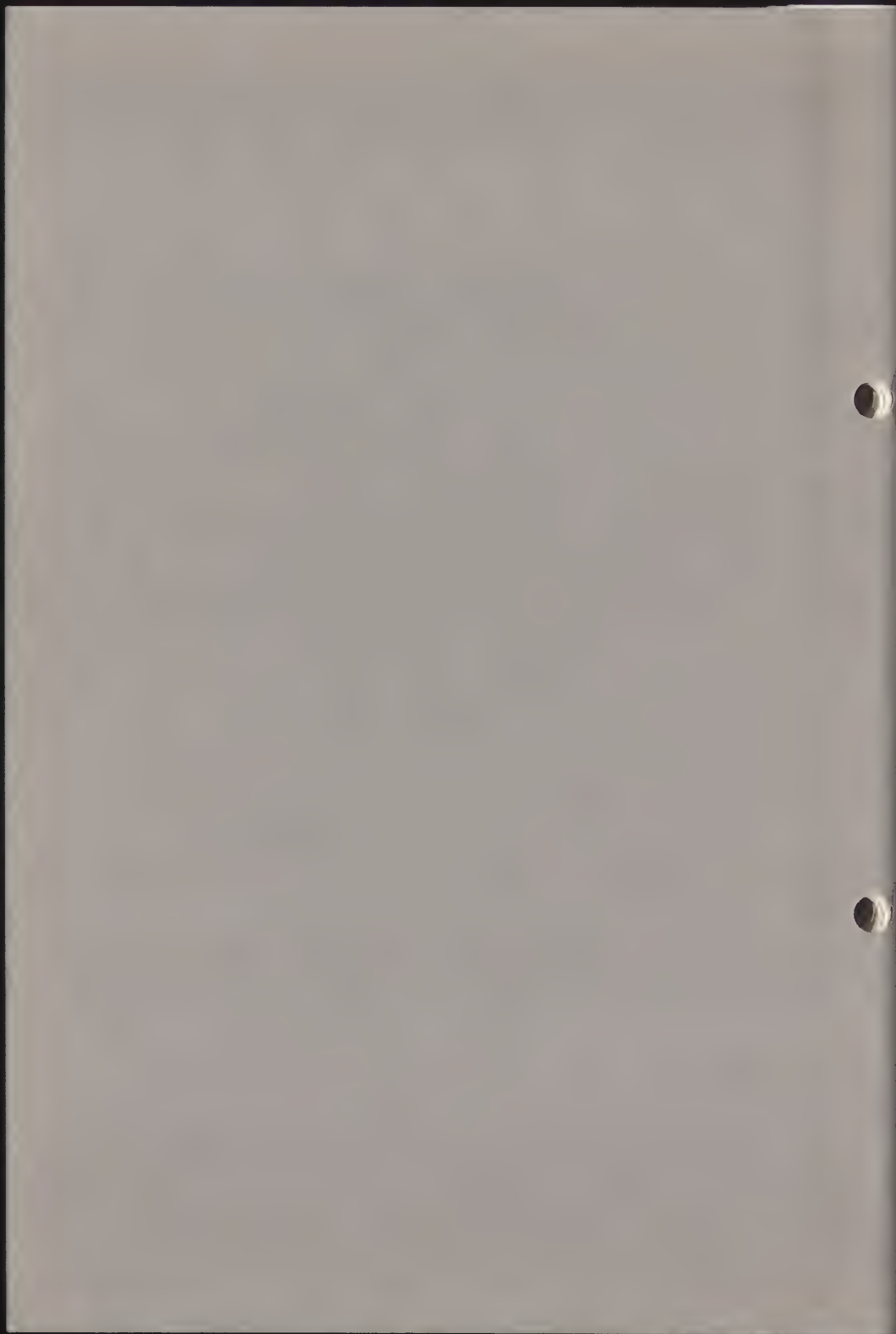
81/14/8

ETUDE EXPERIMENTALE SUR LES FIXATIFS DES
TRACES PULVERULENTS

Françoise Flieder, Roseline Talbot,
Catherine Flieder et Dominique De Reyser

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Documents graphiques et
photographiques



ETUDE EXPERIMENTALE SUR LES FIXATIFS DES TRACES PULVERULENTS

Françoise Flieder, Roseline Talbot, Catherine Flieder et
Dominique De Reyser

Centre de Recherches sur la Conservation des Documents
Graphiques
36 Rue Geoffroy-Saint-Hilaire
Paris 75005
France

Résumé

Nombreux sont les tracés sujets à des détériorations mécaniques provenant le plus souvent de manipulations trop fréquentes. Il peut s'agir aussi bien de fusains, crayons de couleur, pastels que de doubles de carbone ou croquis à la mine de plomb. Il est donc urgent de préserver ces documents d'une valeur inestimable et voués à plus ou moins long terme à une disparition complète du tracé.

Dans ce but, l'effet de deux résines naturelles, quinze résines synthétiques et seize fixatifs du commerce a été expérimenté sur trois papiers de qualité différente.

Il ressort que le Plexisol 550 à 2 % dans l'acétate d'éthyle et l'Elvamide 8061 à 0,5 % dans un mélange méthanol-chlorure de méthylène ont donné d'excellents résultats même après des temps de vieillissement artificiel. Néanmoins, si les pastels réagissent également très bien à l'action de ces résines, l'aspect général de l'oeuvre est souvent modifié.

L'un des soucis majeurs des conservateurs est de préserver la lisibilité d'un texte. Nombreux sont les tracés particulièrement vulnérables qui réclament une protection : dessins, gravures rehaussées de couleurs, fusains, encres corrosives ou pulvérulentes. Les croquis à la mine de plomb, les cartons d'architecte ou de tapisserie posent également des problèmes de permanence ainsi que les annotations ou corrections au crayon sur certains manuscrits. Les doubles de carbone demandent également à être fixés définitivement.

Ces documents se trouvent à la merci de toutes sortes d'agressions mécaniques résultant le plus souvent de manipulations trop fréquentes. Il s'ensuit des pertes de précision de certaines écritures ainsi que des transferts de pigments d'une page à l'autre. Il y a donc nécessité de stabiliser tous ces tracés. La forme d'intervention dépendra, à la fois, de la nature des matériaux à

traiter et du but à atteindre. On distinguera deux cas différents :

- la fixation définitive des tracés instables qui, en fonction des substances employées pour les réaliser, sont sensibles à un simple frottement : fusain, pastel, crayon de couleur, mine de plomb et carbones ;
- la fixation temporaire, avant toute restauration, des encres et des pigments solubles dans l'eau ou sensibles à certains composés chimiques, afin d'éviter qu'ils soient détériorés par les produits utilisés lors de ces traitements.

Dans le présent article, nous n'avons étudié que les fixatifs répondant à la première catégorie, c'est-à-dire ceux devant rester définitivement sur le document, celui-ci étant exclusivement en papier.

MATERIAUX POUVANT ETRE UTILISES POUR FIXER LE TRACE

Les substances destinées à protéger ou à consolider les tracés instables devront être sélectionnées en fonction d'un certain nombre de critères. Elles devront former sur le document un film fin, incolore, mat, n'altérant en aucun cas son aspect. Elles devront être résistantes aux frottements et répondre à certaines qualités de souplesse et d'adhérence. Il sera enfin essentiel qu'elles puissent conserver de façon durable toutes ces propriétés. Le traitement devra pouvoir se réaliser sans risque pour le document et être réversible.

Deux catégories de fixatifs ont été utilisées :

- les substances naturelles, essentiellement d'origine végétale ou animale ;
- les matériaux synthétiques.

1. Les substances naturelles

La plus simple d'entre elles est l'eau. Marylin WEIDNER propose une technique originale qui permet de fixer pastels et fusains après les avoir placés, humidifiés sur une "table à vide". Les pigments s'incrusteront ainsi plus profondément dans le support.

Cependant, la plupart du temps, les documents ont été protégés à l'aide d'un vernis à base de gommes, de résines naturelles ou de cires.

La gomme arabique fut de loin la plus utilisée. Déjà au XVe siècle, les Vénitiens l'employaient pour fixer les fusains (6). On cite également l'utilisation de gomme laque ou de miel.

Plusieurs recettes mentionnent l'emploi de *résinés* telles que sandaraque, mastic, dammar (8) (10).

Enfin des *cires d'abeilles* ou de *cacahuètes* sont citées dans la littérature pour fixer la couche picturale des manuscrits ainsi que des *colles d'esturgeon*, de *parchemin* (7) (9).

Certaines de ces substances continuent à être employées. Cependant dans l'ensemble, elles ont tendance à s'oxyder facilement, à jaunir, à se fragiliser et à perdre de leur souplesse dans le temps. Leur application entraîne parfois une modification de la couleur des pigments (8) ; de plus, elles sont souvent sensibles à l'action des microorganismes.

C'est pour ces différentes raisons que de très nombreux auteurs se sont tournés vers les différentes gammes de résines synthétiques.

2. Les matériaux synthétiques

Ces matières offrent par leur variété, leurs propriétés, ainsi que leurs possibilités de copolymérisation, une grande souplesse d'adaptation permettant de résoudre de nombreux problèmes. L'ensemble des matériaux pouvant être utilisés en tant que fixatifs des tracés pulvérulents se regroupent de la manière suivante :

- Les résines vinyliques

. *les polymères* : l'acétate de polyvinyle, l'alcool de polyvinyle, les formals et les butyrals de polyvinyle ;

. *les copolymères* : acétate de polyvinyle/alcool de polyvinyle, acétate de vinyle/éthylène

- Les résines acryliques

. *les polymères* :

les polyacrylates : polyacrylate de méthyle, polyacrylamide,

les polyméthacrylates : polyméthacrylate de méthyle, de butyle, d'iso-butyle, acide polyméthacrylique ;

. *les copolymères* : acrylate de méthyle/méthacrylate de méthyle, acrylate de méthyle/méthacrylate d'éthyle, acrylate d'éthyle/méthacrylate de méthyle.

- Les résines cellulosiques

. *les esters cellulosiques* : acétate de cellulose ;

. *les éthers cellulosiques* : méthylcellulose, éthylcellulose, benzylcellulose, carboxyméthylcellulose, hydroxyéthylcellulose, éthylhydroxyéthylcellulose

- Les polyamides

- Les résines fluorées

- Les résines alkydes

Cependant, le choix d'un fixatif répondant aux besoins exigés par les problèmes de protection ou de consolidation qui nous préoccupent, nous a amenés à éliminer de cette étude :

- les résines therm durcissables insolubles dans les solvants organiques qui donnent des films durs et cassants ;

- les résines susceptibles de dégager des substances dangereuses pour le support et notamment celles contenant des plastifiants. Ces derniers risquent en effet de disparaître avec le temps, mais aussi de migrer vers le support et de le détériorer ;
- les résines solubles dans l'eau ou les émulsions aqueuses qui nécessitent une élimination totale de l'eau entraînant un temps de séchage trop long. D'autre part, il faut tenir compte du fait que ces substances, au contact d'une humidité excessive, peuvent devenir collantes et attirer la poussière. Notre choix s'est donc orienté vers des résines solubles dans des solvants organiques.

EXPERIMENTATION

Pour notre expérimentation, nous avons contacté des spécialistes ainsi que de nombreuses firmes françaises et étrangères. Nous avons ainsi pu nous procurer toute une gamme de résines correspondant à nos besoins (Annexe 1), auxquelles ont été adjointes deux résines naturelles qui seront testées à titre comparatif (gomme laque et gomme arabique). Nous nous sommes cependant heurtés à des difficultés commerciales quant à certaines résines russes, notamment la VA 2 EGA, le méthylol-polyamide, les résines fluorées (1) dont nous n'avons pu trouver l'équivalent en France.

Parallèlement, nous avons rassemblé toute une série de fixatifs du commerce pour crayons, fusains, pastels et arts graphiques (Annexe 2) que nous avons expérimentés d'une manière analogue aux résines précitées.

1. Choix du solvant

Le choix du solvant est de première importance ; celui-ci peut être en effet à l'origine de certains problèmes de compatibilité avec les pigments et les encres, risquant d'entraîner leur décoloration, leur diffusion ou encore leur solubilisation partielle. Les supports, au contact d'hydrocarbures, de cétones ou d'esters, peuvent acquérir une transparence plus ou moins prononcée. On devra également tenir compte des données définissant les caractéristiques physiques des solvants ainsi que leur toxicité et leur vitesse d'évaporation. La connaissance des paramètres de solubilité permettra de choisir le solvant en fonction de la résine. Nous avons donc été amenés à déterminer pour chacune d'elles le solvant le mieux adapté. Dans ce but, les résines ont été soumises à des tests de solubilité à chaud et à froid dans divers solvants et mélanges de solvants. Nous avons retenu celui qui n'entraînait aucune modification du tracé : bavures, diffusion des couleurs, solubilisation des encres ...

2. Sélection des résines

Des résines et des fixatifs ont été sélectionnés selon trois critères fondamentaux pour la conservation :

Efficacité - Reversibilité - Innocuité vis-à-vis des supports

L'efficacité d'un fixatif est liée à la concentration de la résine dans son solvant. Celle-ci doit être définie de manière à obtenir à la fois une bonne protection et une bonne lisibilité d'un texte, sans pour autant modifier l'aspect du support, sa souplesse et son toucher.

Des solutions de résine de différentes concentrations ont été vaporisées sur des papiers comportant des inscriptions réalisées à l'aide de trois types de carbone*, de fusains, de pastels, de crayons de couleur et de mine de plomb.

Dans l'ensemble, les résultats obtenus furent très satisfaisants. Cependant, nous avons rencontré certaines difficultés pour fixer les pastels. En effet, le choix du solvant compatible avec les différentes couleurs expérimentées est relativement aisé, mais la mise au point d'une concentration idéale de la résine dans le solvant pose un problème. Si celle-ci est faible, le pastel n'est pas fixé, si elle est élevée, la nature du matériau risque d'être très modifiée, son aspect délicat et velouté ayant presque toujours disparu. C'est la raison pour laquelle nous déconseillons de fixer les pastels.

La réversibilité de chacune des résines a été examinée tout de suite après son application sur le papier, ainsi qu'après des cycles de vieillissement artificiel : exposition aux rayons UV et à la chaleur humide.

Afin de se rapprocher le plus possible des conditions d'application en atelier, nous avons opéré de la façon suivante : on pèse avec précision (1/10 de mg) des papiers de qualité différente, puis on les imprègne de résine ; les papiers une fois séchés et pesés, sont trempés pendant quinze minutes dans le solvant approprié afin de dissoudre la résine. On les sèche pendant une nuit à température ambiante et on les pèse une troisième fois afin de s'assurer que toute la résine a bien été éliminée.

Les problèmes liés à l'entassement des documents en bibliothèque, en présence parfois d'une forte humidité, ont également été abordés dans cette étude. Ainsi, nous avons voulu tester le pouvoir d'adhésion des papiers imprégnés de résine. Des échantillons traités ont été maintenus sous presse en atmosphère humide (étuve à 35°C et 80 % H.R.) pendant huit jours.

Afin de s'assurer de l'innocuité des produits vis-à-vis des supports, une première approche a été réalisée en effectuant quelques tests sur la résistance physique d'un papier traité par un grand nombre de résines et fixatifs retenus après examen de leur réversibilité.

* Armor - Pelikan - Korès

Nous avons sélectionné ainsi six résines* et trois fixatifs** du commerce qui ont fait l'objet d'une étude approfondie dont nous donnons ici une description sommaire.

3. Protocole d'analyse

3.1. *Choix de la méthode d'imprégnation*

Trois méthodes d'imprégnation ont été expérimentées. Le but recherché était d'obtenir l'absorption la plus homogène possible de la résine par le support et par là même une dispersion minimale des résultats de nos essais.

- La première méthode utilise le filmographe du Dr BLADE et permet, à l'aide d'une lame métallique que l'on fait glisser dans les rainures d'un support fixe, d'étaler la résine en solution (d'une épaisseur homogène et déterminée) sur le papier maintenu sur ce même support.

- La deuxième méthode est la vaporisation que l'on effectue à environ 25 à 30 mm de la feuille de papier.

- la troisième méthode consiste à tremper les feuilles de papier quelques minutes dans la solution de résine, puis à les sécher à plat sur des plaques de verre.

A partir de tests de contrôle de la résistance mécanique, nous nous sommes rendus compte que trempage et vaporisation donnaient des résultats homogènes et similaires. La méthode du Dr BLADE est de réalisation plus délicate et présente des résultats plus dispersés.

Cependant, la technique du trempage constitue à nos yeux une méthode d'expérimentation plus sévère car le papier absorbe une quantité plus importante de résine que lors d'une vaporisation. Aussi, avons-nous utilisé ce procédé de manière générale pour tester à la fois les résines et les fixatifs du commerce vendus en aérosol***. Pour ces derniers, le trempage a été effectué dans les solutions contenues dans les bombes après élimination du gaz vecteur.

* Polyuréthane aliphatique TP 71 ; Elvax 40 ; Elvamide 8061 ; Plexisol P 550, Paraloid B 72, gomme laque.

** Fixatif Latour ; Fixatif Lefranc-Bourgeois ; Fixatif acrylique Lascaux.

*** Il peut paraître surprenant d'employer en immersion des produits vendus pour être utilisés en aérosol. Nous avons cependant tenu à faire cet essai, de manière à se mettre dans les conditions d'emploi les plus mauvaises, c'est-à-dire celles où l'opérateur aurait pulvérisé une trop grande quantité de fixatif sur le document.

3.2. *Choix des tests d'expérimentation*

Les tests ont été réalisés sur des papiers imprégnés avec les solutions de résine mises au point ainsi qu'avec les fixatifs du commerce.

Nous avons établi un échantillonnage aussi large que possible des différentes sortes de supports comprenant :

- un papier vélin de très belle qualité : 100 % pâte de chiffon
- un papier d'édition : 100 % pâte chimique blanchie
- un papier journal : 80 % pâte mécanique de sapin,
10 % pâte de sapin bisulfite écrue
10 % pâte de sapin bisulfite blanchie

Les tests ont été effectués avant et après deux types de vieillissement artificiel :

- un vieillissement artificiel à la chaleur humide (80°C à 60 % H.R. pendant quatre jours) qui entraîne des réactions d'hydrolyse et d'oxydation ;
- un vieillissement artificiel à la lumière (96 heures d'exposition pour chaque face au rayonnement d'une lampe à vapeur de Hg) provoquant des réactions photo-chimiques.

Nous avons retenu d'une part des tests optiques qui permettent d'analyser les modifications de couleur et d'opacité (normes Afnor NFQ 03 008 et NFQ 03 006), d'autre part des tests de résistance mécanique (appareils Lhomargy dans une salle conditionnée à 23°C et 50 % H.R.) : résistance à la traction avec calcul du module d'élasticité et résistance à l'éclatement (normes Afnor NFQ 03 004, 03 053).

Des mesures du taux d'acidité (Tappi T 435 m 52) ont été réalisées parallèlement.

4. Résultats

4.1. *Les résines naturelles*

Deux résines ont donc été examinées :

- la gomme arabique à 3 % dans l'eau donne de bons résultats à tous les tests, cependant son pouvoir hygroscopique risque de provoquer des dangers qu'il est bon d'éviter ;
- la gomme laque à 1 % dans l'alcool éthylique (tableau 3) diminue l'élasticité et la blancheur du papier vélin et du papier journal. Par ailleurs, cette résine n'est plus réversible après un vieillissement d'une semaine à 80°C et 60 % H.R.

Nous n'avons donc pas cru devoir retenir de résines naturelles.

4.2. *Les résines synthétiques*

Un grand nombre de résines ont été éliminées car leur réversibilité était mauvaise.

Ce fut le cas en particulier pour l'Acrylharz 742-33 A, le Syntacryl SC 105, le Calaton CA, l'Acryfirnis P 550 35 mat. De plus, cette résine présente l'inconvénient de contenir un agent matant qui entraîne un dépôt blanc à la surface du papier.

D'autre part, les premiers tests de résistance physico-chimique effectués sur un papier d'édition ont montré que quelques-unes des résines examinées provoquaient un affaiblissement de certaines constantes. C'est ainsi, par exemple, que l'acétate de cellulose et l'acétate de polyvinyle ont occasionné une diminution de la souplesse du papier.

Pour les autres produits retenus, tous les tests de résistance physico-chimique ont été réalisés sur les trois papiers de qualité différente ; les résultats obtenus étant si nombreux, il n'a pas été possible de les faire tous figurer ici, nous ne présentons donc que ceux qui nous ont paru les plus intéressants :

Il ressort de cette étude les conclusions suivantes :

- Deux produits sont à retenir, le Plexisol 550 en solution à 2 % dans l'acétate d'éthyle et l'Elvamide 8061 en solution à 0,5 % dans un mélange 50/50 de méthanol et de chlorure de méthylène. Dans les deux cas, tous les résultats des tests sont très satisfaisants (tableaux 1 et 2). La réversibilité est excellente (légèrement meilleure cependant pour Plexisol 550 que pour Elvamide 8061 après vieillissement d'une semaine à 80°C et 60 % H.R.).

- Le Polyuréthane aliphatique à 1 % dans un mélange 50/50 toluène-alcool isopropylique et l'Elvax 40 à 1 % dans un mélange 50/50 acétate d'éthyle-trichloréthylène, provoquent tous les deux une diminution de l'élasticité des trois papiers, mais l'Elvax 40 entraîne en plus un jaunissement particulièrement net sur le papier journal vieilli à la chaleur humide.

- Le Paraloid B 72 à 1,5 % dans l'acétate d'éthyle est de loin la résine qui a le moins bien réagi : perte de souplesse assez importante et jaunissement de tous les papiers traités, même avant vieillissement artificiel. Par contre, c'est la seule résine qui diminue l'acidité des papiers traités.

Aucune adhérence n'a pu être constatée entre les papiers imprégnés de ces différentes résines et maintenus sous presse en présence d'une forte humidité.

4.3. Les fixatifs du commerce

Ces fixatifs, tous réversibles, ont été testés en premier sur le papier d'édition par vaporisation et trempage. Cette dernière méthode d'imprégnation que l'on peut assimiler à la vaporisation d'une grande quantité de résine, nous a amenées à retrancher de ces essais certains fixatifs qui ont provoqué des effets

indésirables sur les supports que nous voulions tester : taches jaunes, papiers devenus transparents, brillants ou collants ou encore gondolés. Il s'agit en particulier de : Van Eyck, Krylon, Delacroix, Rosalba, Humlec, Let-Fix, Profix, Scotch et Blair.

Par ailleurs, le fixatif Dalbe mat a occasionné le dépôt de son agent matant sur le support sous forme d'une poudre blanche. Le fixatif Tallens a rendu le papier très collant.

Pour les trois fixatifs retenus, on a examiné en détail, comme pour les résines, le comportement des trois papiers traités.

Le fixatif Lascaux (talbeau 4) est certainement celui qui a donné les meilleurs résultats. On constate cependant qu'il a entraîné un jaunissement assez important des trois papiers.

Les fixatifs Sennelier-Latour et Lefranc-Bourgeois ne peuvent pas être retenus en fonction de la perte importante de l'élasticité des papiers et du jaunissement qu'ils provoquent particulièrement sur le papier journal.

Signalons qu'après 8 jours de vieillissement à 80°C et 60 % H.R., la résine Lefranc-Bourgeois n'est plus réversible.

Dans l'ensemble, les résultats obtenus avec les fixatifs du commerce sont nettement inférieurs à ceux obtenus avec les résines.

o

o o

Ce travail qui devait définir la meilleure façon de fixer définitivement les tracés pulvérulents a répondu au but recherché.

Il ressort en effet de ces résultats que, si les résines naturelles examinées n'ont pas toujours donné entière satisfaction, par contre deux résines synthétiques, le Plexisol 550 et l'Elvamide 8061 semblent résoudre bien des problèmes, particulièrement en ce qui concerne le fusain, la mine de plomb et les carbones. La stabilisation des pastels est beaucoup plus délicate, car même si le solvant n'endommage pas les couleurs, l'aspect final de l'oeuvre traitée sera toujours modifié.

Signalons cependant que les deux résines retenues doivent être utilisées avec beaucoup de prudence ; avant tout traitement, des essais ponctuels doivent être faits afin de s'assurer que la résine et son solvant sont compatibles avec les différents constituants de l'oeuvre et qu'il n'y a pas de risque de solubilisation des encres ou des couleurs.

- (1) BELENKAYA (N.G.) and STRELTOSOVA (T.N.), *Application of methylol polyamide glue PFE-2/10 in the restoration and seamless reinforcement of books and documents*, New Methods for the Restoration and Preservation of Documents and Books (translated from Russian) Jerusalem, Israël, Program for scientific translations, 1964, p. 79-86
- (2) BRANDRUP (J.); IMMERGUT (E.H.), Ed., *Polymer Handbook*, 2nd ed., New-York-London-Sydney-Toronto : Wiley Interscience, 1975
- (3) DE WITTE (E.) et GOESSENS-LANDRIE (M.), *The Structure of "old" and "new" Paraloid B 72*, I.C.O.M., Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978
- (4) FELLER (R.L.), *Standards in the evaluation of thermoplastic resins*, I.C.O.M., Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978
- (5) FELLER (R.L.) and CURRAN (M.), *Solubility and crosslinking characteristics of ethylene/vinylacetate copolymers*, Bulletin of the American Group, International Institute for Conservation of Historic and Artistic Works, octobre 1970, vol. 11, n° 1, p. 42-45
- (6) LAVALLEE (P.), *Les Techniques du dessin : leur évolution dans les différentes écoles de l'Europe*, 2e éd. revue et corrigée, Paris, Van Oest, 1949
- (7) MARCONI (Bohdan), *Some tests on the use of wax for fixing flaking paint on illuminated parchment*, Studies in Conservation, May 1962 vol. 7, n° 1, p. 17-21
- (8) MOKRETZOVA (I.P.), *Les Problèmes de la restauration des manuscrits médiévaux sur parchemin*, Restauration, Recherche et Sauvegarde des Oeuvres d'Art Graphique, Moscou, 1977, p. 31-38
- (9) NOGID (I.C.), *La Restauration du tableau de Matisse "le Café Arabe"*, Soobschenija, Moscou, 1970, 26, p. 169-176
- (10) ROMAIN (A.), *Nouveau manuel complet du fabricant de vernis de toute espèce*, Nette édition revue et augm., Paris, Encycl. Roret, 1977
- (11) SALZ (Karl); SKRIVANEK (Ladislav), *Application of copolymers of polyvinylacetals as a means for protection, preservation, restoration, stabilization, hydrophobization of papyrus, papers, books and/or manuscripts*, United States Patent n° 3698925, 3 p., 1972
- (12) TORRACA (G.), *Solubility and solvents for conservation problem*, Rome, Inter. Centre for the Study of the Pres. and Rest., 1975
- (13) WACHTER (Otto), *Fixierungsmöglichkeiten für Eisengallüstinten bei Chemischen Instandsetzungsarbeiten*, Archives et Bibliothèques de Belgique, n° spécial 12, Bruxelles, 1974, p. 223-233
- (14) WEIDNER (Marilyn), *A vacuum table for use in paper conservation*, Bulletin of the A.I.C., 1974, vol. 14, n° 2, p. 115-122

EFFET DE L'ELVAMIDE 8061 SUR TROIS PAPIERS DE QUALITE DIFFERENTE

	Longueur de rupture en mètres		% allongement à la rupture		Résistance éclat.	Blanchéur	Opacité	pH
	ST	SM	ST	SM				
Panier vëlin témoin	2125	3474	5,39	3,96	1,8	78,4	98,3	6,5
Panier vëlin traité	2218	3698	5,51	4,38	2,1	78,6	98,4	6,4
Panier vëlin témoin vieilli 80°C, 60 %	2096	3286	4,82	3,27	1,8	76,9	99	6,5
Panier vëlin traité vieilli 80°C, 60 %	2242	3939	4,61	3,67	2,0	75,2	99	
Panier vëlin témoin vieilli UV 96 heures	2021	3512	4,57	3,50	1,9	73,3	99,4	5
Panier vëlin traité vieilli UV 96 heures	2093	3601	3,85	3,12	2	72	99,5	5
Panier édition témoin	2645	6758	4,98	1,71	2,3	84,6	91,7	5,4
Panier édition traité	2768	6592	6,60	2,09	2,4	83,5	92,1	5,2
Panier édition témoin vieilli 80°C, 60 %	2599	6625	4,44	1,66	2,2	76,2	95,8	5,2
Panier édition traité vieilli 80°C, 60 %	2837	6707	5,47	1,84	2,4	75,6	95,6	5,3
Panier édition témoin vieilli UV 96 heures	2593	6305	4,19	1,68	2,3	81,7	92,8	4,6
Panier édition traité vieilli UV 96 heures	2934	6845	5,69	2,03	2,4	82	92,8	4,8
Panier journal témoin	1595	3392	1,47	0,85	1	53,3	96,7	5,7
Panier journal traité	1951	3980	1,71	0,88	1,2	52,2	98,4	5,7
Panier journal témoin vieilli 80°C, 60 %	1506	3493	1,2	0,65	1	47	99,3	5,8
Panier journal traité vieilli 80°C, 60 %	1612	3395	1,27	0,76	1,1	47	99,1	5,3
Panier journal témoin vieilli UV 96 heures	1303	3025	1,10	0,65	0,9	35	99,6	4
Panier journal traité vieilli UV 96 heures	1821	3911	1,21	0,86	1,2	36,1	95,4	4

Panier vëlin : 100 % pâte de chiffon de coton

ST = sens travers

Panier édition : 100 % pâte chimique blanche

SM = sens machine

Panier Journal : 80 % pâte mécanique de sapin

10 % pâte de sapin bisulfite écriue

10 % pâte de sapin bisulfite blanche

EFFET DU PLEXISOL P550 SUR TROIS PAPIERS DE QUALITE DIFFERENTE

	Longueur de rupture en mètres		% allongement à la rupture		Résistance éclat.	Blancheur	Opacité	pH
	ST	SM	ST	SM				
Papier vélin témoin	2125	3474	5,39	3,96	1,8	78,4	98,3	6,5
Papier vélin traité	2514	4217	4,98	3,90	2,2	76,9	98,1	
Papier vélin témoin vieilli 80°C, 60 %	2096	3286	4,82	3,27	1,8	76,9	99	6,5
Papier vélin traité vieilli 80°C, 60 %	2477	4356	4,35	3,83	2,2	72,7	98,8	
Papier vélin témoin vieilli UV 96 heures	2021	3512	4,57	3,50	1,5	73,3	99,4	5
Papier vélin traité vieilli UV 96 heures	2432	4213	3,80	2,70	2,2	75,9	99,8	5,2
Papier édition témoin	2645	6758	4,98	1,71	2,3	84,6	91,7	5,4
Papier édition traité	3004	7269	6,15	2,14	2,7	82,8	91,2	5,3
Papier édition témoin vieilli 80°C, 60 %	2599	6625	4,44	1,66	2,2	76,2	95,8	5,2
Papier édition traité vieilli 80°C, 60 %	2866	7101	5,02	1,85	2,5	75,8	94,8	5,3
Papier édition témoin vieilli UV 96 heures	2598	6305	4,19	1,68	2,3	81,7	92,8	4,6
Papier édition traité vieilli UV 96 heures	3019	6826	5,63	1,88	2,6	80,6	92,5	5
Papier Journal témoin	1595	3392	1,47	0,85	1	53,3	98,7	5,7
Papier Journal traité	1720	3865	1,12	0,75	1,1	51,8	98,2	5,8
Papier Journal témoin vieilli 80°C, 60 %	1506	3493	1,2	0,65	1	47	99,3	5,8
Papier Journal traité vieilli 80°C, 60 %	1690	3668	1,18	0,77	1,1	46,2	99	5,5
Papier Journal témoin vieilli UV 96 heures	1303	3025	1,10	0,65	0,9	35	99,6	4
Papier Journal traité vieilli UV 96 heures	1639	3391	1,21	0,66	0,80	37,6	99,5	3,9

Papier vélin : 100 % pâte de chiffon de coton

Papier édition : 100 % pâte chimique blanche

Papier Journal : 80 % pâte mécanique de sapin

10 % pâte de sapin bisulfite écriue

10 % pâte de sapin bisulfite blanche

ST = sens travers

SM = sens machine

EFFET DE LA GOMME LAQUE SUR TROIS PAPIERS DE QUALITE DIFFERENTE

	Longueur de rupture en mètres		% allonge- ment à la rupture		Résis- tance éclat.	Blan- cheur	Opa- cité	pH
	ST	SM	ST	SM				
Papier vélin témoin	2125	3474	5,39	3,96	1,8	78,4	98,3	6,5
Papier vélin traité	2009	3589	6,40	4,73	2	77,4	98,3	6,3
Papier vélin témoin vieilli 80°C, 60 %	2096	3286	4,82	3,27	1,8	76,9	99	6,5
Papier vélin traité vieilli 80°C, 60 %	2046	3461	3,47	2,81	1,8	72,7	99	6,2
Papier vélin témoin vieilli UV 96 heures	2021	3512	4,57	3,50	1,9	73,3	99,4	5
Papier vélin traité vieilli UV 96 heures	2125	3308	3,85	2,91	1,8	71,9	99,5	5
Papier édition témoin	2645	6758	4,98	1,71	2,3	84,6	91,7	5,4
Papier édition traité	2746	6713	5,36	1,86	2,3	83,8	92,1	5,1
Papier édition témoin vieilli 80°C, 60 %	2599	6625	4,44	1,66	2,2	76,2	95,8	5,2
Papier édition traité vieilli 80°C, 60 %	2629	6861	4,54	1,63	2,1	76,6	95,3	5
Papier édition témoin vieilli UV 96 heures	2598	6305	4,19	1,68	2,3	81,7	92,9	4,6
Papier édition traité vieilli UV 96 heures	2684	6698	4,60	1,63	2,1	85,3	93	4,8
Papier journal témoin	1595	3392	1,47	0,85	1	53,3	98,7	5,7
Papier journal traité	1718	3643	1,35	0,74	1,2	51,4	98,5	5,4
Papier journal témoin vieilli 80°C, 60 %	1506	3493	1,2	0,65	1	47	99,3	5,8
Papier journal traité vieilli 80°C, 60 %	1744	3410	1,21	0,65	0,9	46,7	98,9	
Papier journal témoin vieilli UV 96 heures	1303	3025	1,10	0,65	0,8	35	99,6	4
Papier journal traité vieilli UV 96 heures	1627	3178	1,15	0,61	0,9	34,9	99,2	4

Papier vélin : 100 % pâte de chiffon de coton

ST = sens travers

Papier édition : 100 % pâte chimique blanche

SM = sens machine

Papier journal : 80 % pâte mécanique de sapin

10 % pâte de sapin bisulfite écorue

10 % pâte de sapin bisulfite blanche

T A B L E A U N ° 4

L'EFFET D'UN FIXATIF DU COMMERCE (LASCAUX) SUR TROIS PAPIERS DE QUALITE DIFFERENTE

	Longueur de règle en mètres		% allonge- ment à la rupture		Résis- tance éclat.	Blan- cheur	Opa- cité	pH
	ST	SM	ST	SM				
Papier velin témoin	1994	3278	4,78	3,66	1,8	78,7	98,4	6,6
Papier velin traité	2384	4033	4,96	4,54	2	77,8	97,7	6,4
Papier velin témoin vieilli 80°C, 60 %	1913	3125	4,50	3,38	1,6	75,2	99,1	6,5
Papier velin traité vieilli 80°C, 60 %	2480	4477	3,87	3,27	2,1	64,9	99,2	6,5
Papier velin témoin vieilli UV 96 heures	2002	3898	4,05	2,83	1,7	75,4	99	5,1
Papier velin traité vieilli UV 96 heures	2664	4317	3,96	3,89	2	71,4	99,2	5,1
Papier édition témoin	2645	6758	4,98	1,71	2,3	84,6	91,7	5,4
Papier édition traité	2833	6952	6,10	2,27	2,6	82,2	90,3	5,1
Papier édition témoin vieilli 80°C, 60 %	2599	6625	4,44	1,66	2,2	76,2	95,8	5,2
Papier édition traité vieilli 80°C, 60 %	2712	6638	4,14	1,72	2,4	73,8	94,1	5
Papier édition témoin vieilli UV 96 heures	2598	6305	4,19	1,68	2,3	81,7	92,9	4,6
Papier édition traité vieilli UV 96 heures	2919	6852	5,51	1,97	2,5	81,4	91	5
Papier journal témoin	1595	3392	1,47	0,85	1	53,3	98,8	5,7
Papier journal traité	1758	4111	1,49	1,13	1,1	49,3	97	5,7
Papier journal témoin vieilli 80°C, 60 %	1506	3493	1,2	0,65	1	47	99,5	5,8
Papier journal traité vieilli 80°C, 60 %	1734	3880	1,07	0,76	1,7	42,5	98,4	5,5
Papier journal témoin vieilli UV 96 heures	1303	3025	1,10	0,65	0,9	35	99,6	4
Papier journal traité vieilli UV 96 heures	1882	3839	0,93	0,66	0,9	32,8	99,5	3,8

Papier velin : 100 % pâte de chiffon de coton

Papier édition : 100 % pâte chimique blanche

Papier journal : 80 % pâte mécanique de sapin

10 % pâte de sapin bisulfite écorce

10 % pâte de sapin bisulfite blanche

ST = sens travers

SM = sens machine

ANNEXE 1
LISTE DES RESINES EXPERIMENTEES

81/14/8-15

Composition chimique	Solvant	Nom commercial	Marque
RESINES SYNTHETIQUES <u>Résines vinyliques</u> <i>Polymères</i>			
acétate de polovynyle	0,25 % dans acétate d'éthyle 2 % " " " 2 % " " " 2 % " " "	Rhodopas M 60 A Howilith 30 Howilith 35/75 Howilith 50	Rhône Poulenc Hoechst
<i>Copolymères</i> acétate de vinyle/éthylène	1 % dans 50/50 acétate d'éthyle/ trichloréthylène	Elvax 40	Dupont de Nemours
<u>Résines cellulosiques</u> acétate de cellulose	0,25 % dans 50/50 acétone/acétate d'éthyle	Acétate de cellulose R 1 B	Rhône Poulenc
<u>Résines acryliques</u> <i>Polymères</i>			
méthacrylate de butyle	2 % acétone 2 % acétate d'éthyle	Acryfirmis P 550 35 mat Plexisol P 550	Lascaux Rohm G m b H Lascaux
résine à base de méthacrylate d'éthyle	2 % alcool éthylique	Acrylharz 742 33 A	
<i>Copolymères</i> acrylate d'éthyle/méthacrylate de méthyle	2 % acétate d'éthyle	Synthacryl S C 105	Hoechst
acrylate d'éthyle/méthacrylate d'éthyle	1,5 % acétate d'éthyle	Paraloid B 72	Rohm et Haas
méthacrylate de butyle/méthacrylate d'éthyle	2 % acétone	Acryl Glasur 40 X	Lascaux
<u>Résines polyamides</u> nylon 6/6	1,5 % dans 1/5 éthanol/eau 0,5 % dans 50/50 méthanol/ chlorure méthylène	Calaton CA Elvanide 8061	I.C.I. Dupont de Nemours
<u>Résines polyuréthanes</u>	1 % dans 50/50 toluène/alcool isopropylique	Polyuréthane aliphatique TP 71	Dicas Chimie

A N N E X E 2

LISTE DES FIXATIFS DU COMMERCE EXPERIMENTES1. En aérosol

HUMLEC	Research Dev. Indus.
DALBE MAT	Fabrique en R.F.A.
LET FIX fixative Cristal	Mecanorma
FIXATIF n° 1306	Krylon
FIXATIF n° 16	Talens
BLAIRNOODOR	Blair Arts Products - U.S.A.
PRO FIX	Talas (N.Y.)
SCOTCH	3 M
VERNACRYL	Ets Robert
FIXATIF CRISTAL n° 1326	Lefranc-Bourgeois
(à base d'acétate de vinyle)	

2. En solution

VAN EYCK	Van Eyck, Munich
ROSALBA, réf. 941	Lefranc-Bourgeois
FIXATIF n° 661	Lefranc-Bourgeois
FIXATIF DELACROIX	Sennelier
FIXATIF LATOUR	Sennelier
(à base de nitro-cellulose)	
LASCAUX-FIX	Lascaux
(à base de méthacrylate d'iso-butyle)	

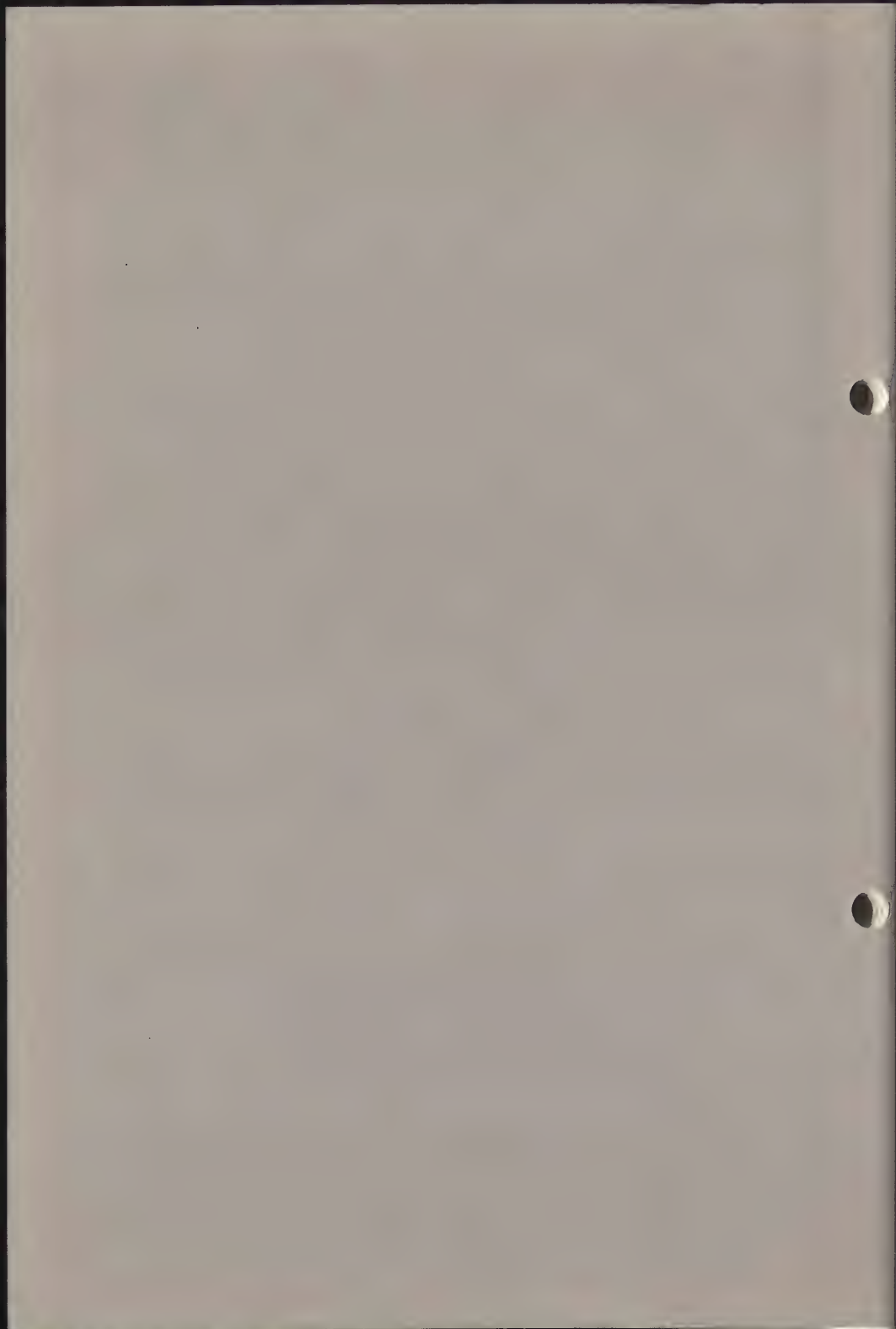
81/14/9

HYDROXY PROPYL CELLULOSE, A MULTIPURPOSE
CONSERVATION MATERIAL

Judith Hofenk-de Graaff

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



HYDROXY PROPYL CELLULOSE, A MULTIPURPOSE CONSERVATION MATERIAL

Judith Hofenk-de Graaff

Central Research Laboratory for Objects of Art and Science
Gabriël Metsustraat 8
1071 EA Amsterdam
the Netherlands

Abstract

A new conservation material, hydroxy propyl cellulose is tested. The special properties of this material, being soluble in water as well in polair organic solvents are expressed. Aging tests are carried out. A number of case-histories shows the multi purpose properties of the material.

Introduction

Some years ago we discovered a trade product, named Klucel^R, made by Hercules inc, Delaware, USA. This product, containing hydroxy propyl cellulose seemed to us a very useful material for sizing fragile papers, particularly for those where water had to be avoided. Hydroxy propyl cellulose belongs to the group of cellulose ethers like methyl cellulose, which has been used already for years by paper conservators as a glue and sizing material. The great advantage of hydroxy propyl cellulose is, that it is soluble in water as well as in polair organic solvents. This properties make it possible to combine aqueous and nonaqueous conservation methods. Having made preliminary experiments for various purposes a research programm was started particularly to test the aging properties of hydroxy propyl cellulose used as a sizing material.

Research

A research project was originally started for the conservation of Mattisses collage "La Peruche et la sirene" of the Stedelijk Museum at Amsterdam. The coloured parts of the collage had to be removed and replaced on a new paper. This paper, a 100% rag paper, made by Van Gelder, had a very soft structure and the conservator thought it be better to size the paper before the coloured parts were replaced. For this purpose various

sizing materials were tested and within the frame of the testing of the hydroxy propyl cellulose research, the following materials were choosen.

Materials

Sodium carboxy methyl cellulose, medium viscosity 2%
 Sodium carboxy methyl cellulose, high viscosity 2%
 gelatin 0,24%
 Klucel G (hydroxy propyl cellulose) 2%
 Tylose MH20 (methyl cellulose) low viscosity 2%
 Tylose MH200 xp (methyl cellulose) high viscosity 2%

Paper

100% RAG paper, 200 gramm/m², made by Van Gelder, Holland

Procedure

Solutions in water of the above mentioned materials were brushed on the rag paper. After drying for 3x 24 hours the impregnated paper was aged in a dry oven for 3x 24 hours at 105°C (after NEN 1855=ASTM).

Testing

The samples are tested before and after aging with the following methods

1. Folding endurance, with the Köhler Molin apparatus with a load of 200 gramms, in machine and cross direction
2. Tensile breaking strength and elongation in machine and cross direction, after ASTM D 828
3. Tear strength in machine and cross direction, after ASTM D 689
4. Bursting strength after ASTM D 774
5. Water absorption, Cobb test, after ASTM D 2045
6. Brightness, after ASTM D 985

Results

Table I gives the results of the tests.

xa = unaged samples

xb = aged samples

% = deterioration, calculated $\frac{xa - xb}{xa} \times 100\%$

m = machine direction

d = cross direction

1 = untreated 100% rag paper

2 = sodium carboxy methyl cellulose medium viscosity

3 = sodium carboxy methyl cellulose high viscosity

4 = gelatin

5 = Klucel G

6 = Tylose MH20

7 = Tylose MH200

Discussion of the results

There is no significant difference between the tested sizing materials.

All the materials have a positive effect on the aging properties of the tested paper under the above mentioned conditions. The aging test at 105°C is not an ideal aging method, but to compare various materials it is a useful method. Correlation with natural aging stays difficult. The only significant difference under these conditions is the water absorbance of the hydroxy propyl cellulose comparing with other tested materials. However, under normal climatic conditions in the museum this is not a disadvantage.

Comparing the hydroxy propyl cellulose with the other tested materials, which are used already for years with success in paper conservation practice, one can conclude, that it can be used as well as the other materials.

The advantage of hydroxy propyl cellulose lies in its solubility in water as well as in polair organic solvents.

Properties of hydroxy propyl cellulose, Klucel^R (1,2)
chemical composition: Hydroxy propyl cellulose is made by reacting alkali cellulose with propylene oxide. The propylene oxide is substituted to the cellulose through an ether linkage at the three reactive hydroxyls present on each androglucose monomer unit of the cellulose chain. It is suggested that all the primary hydroxyls on the cellulose chain have been substituted and that only the reactive groups remaining are secondary hydroxyls.

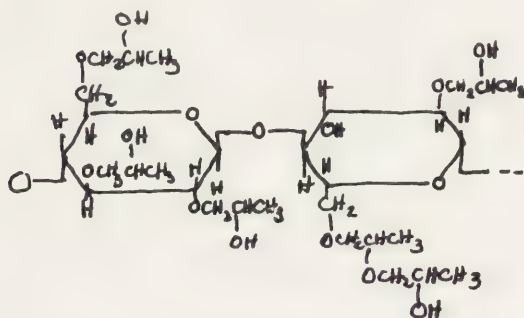


fig. 1
 Idealized structure
 with molair-
 substitution (M.S.)
 of 3,0

Solubility: It is soluble in water below 40°C, in many polair organic solvents, e.g. methyl, ethyl and isopropyl alcohol, methyl cellosolve, cellosolve, chloroform, dioxane, dimethylsulfoxide, demethyl formamide, cyclohexanon. In some mixtures of polair and nonpolair organic solvents, e.g. acetone:water, 9:1; benzene:methanol, 1:1; toluene: ethanol, 3:2.

Surface activity is high, the interfacial tensions of the solutions are low.

Compatible with other water soluble polymers like CMC, methyl cellulose, starch, gelatin, natural gums, poly-ethyleneglycols, etc.

It is also compatible with many latexes as emulsions in water, like polyvinylacetate (Mowilith^R) and methyl and butyl acrylates (Plextol^R).

Flexibility: Films made of hydroxy propyl cellulose are very flexible. The flexibility increases with the molecular weight. The films are thermoplastic and can be used for heatsealing.

Plasticizers: Hydroxy propyl cellulose does not contain any plasticizer, however, plasticizers such as glycerin and poly ethylene glycol can be used.

Effect of pH: Hydroxy propyl cellulose is a nonionic polymer and the solution in water is not effected by changes in pH over a range of 2 to 11.

Stability of the solution: an aqueous solution has the best stability when the pH is held between 6,0 and 8,0. The aqueous solution is susceptible to both chemical and biological degradation. The solutions, however, are compatible with various preservatives, e.g. formaldehyde, phenyl-mercuric acetate, sodium omadine, thiopropionic acid, sodium benzoate and propionate and the Na, K and Ca salts of sorbic acid.

Humidity: the moisture content at 20°C and 50% RH is 4% at 20° and 84% RH, 12%. There is no blocking of films at roomtemperature and 90% RH.

Case histories

1. Drawings of charcoal and red ocre. 17th century

A series of drawings on very deteriorated blue paper had to be restored. The paper was dark brown and very brittle. pH was 4,0. After preliminary tests it became clear that it was impossible to wash or bleach the paper in aqueous solutions. From the point of view of conservation and esthetical a treatment was necessary. We decided to make use of the special properties of Klucel, being soluble in cold water and not in hot water above 45°C. (Before starting the whole procedure, we carried out the experiment with a self made pastel drawing.) A drawing was sprayed with 2% Klucel G in ethyl alcohol. Then it was bleached in chlrodioxyde gas. After bleaching, to remove dirt, the rests of the bleaching procedure and some soluble acids, the drawing was washed with hot water of + 60°C for 5 minutes. The effect was remarkable. The paper was blue again and the charcoal drawing did not loose any of its pigment.

After drying the drawing was deacidified with a solution of methyl magnesium carbonate in methyl alcohol. The paper of the drawing was still very brittle and had to be relined. But water had to be avoided.

Therefore a new relining method was developed.

Relining method. A sheet of Renova paper, an artificial "Japanese" paper, made of viscose rayon was impregnated with a 5% solution Klucel J (a filmforming type of hydroxy propyl cellulose) mixed with 1/15 part of Mowilith DMC2 (polyvinylacetate).

The impregnation was carried out on a Teflon sheet (or siliconpaper). After drying a thin film was formed on one side of the Renova paper. The impregnated sheet of Renova paper with the film on top was placed on a vacuum table. The drawing was wetted with ethyl alcohol and laid on the Renova paper. The sandwich covered with a sheet of Teflon coated fabric and the vacuum pump putted on. The ethyl alcohol dissolved partly the glue layer and by the pressure the two layers are fixed perfectly to each other. The relining was finished when all the ethyl alcohol was evaporated.

2. Conservation of a 17th century map (2x3 meter)

The map was in very bad condition. The surface was broken into pieces. The linen lining was completely degraded. This lining had to be removed and replaced by a new one.

The surface of the map was protected by glueing sheets of Japanese paper with 5% Klucel G in water. The lining was removed with warm water (Klucel does not dissolve in warm water). A new lining was glued on the map with starch. After completing the conservation work, the protecting layer on the frontside was removed with ethyl alcohol, because the starch glue of the new lining does not dissolve in the ethyl alcohol.

3. Sizing

Solutions of 1-2% Klucel G are already used with success as a sizing material.

Particularly in these cases where water had to be avoided, e.g. pastel. There is no optical change of the surface. It can be combined with a deacidification treatment using methyl magnesium carbonate. In this case the Klucel is dissolved in methyl alcohol.

4. Consolidation of deteriorated leather

A solution of Klucel G in ethyl alcohol is successfully used for the impregnation of leatherbindings deteriorated by "red rot". This is carried out by Anthony Cains, Trinity College Library, Dublin (personal communication).

Conclusions

Hydroxy propyl cellulose can be used with success in a great number of special problems in paper conservation. The above mentioned cases are only a selective part of the possibilities of the material. However, the inventive paper conservation can find more applications in connection to the special properties of hydroxy propyl cellulose.

References

1. Klucel, hydroxy propyl cellulose, chemical and physical properties. Hercules inc. 910 Marbet Street, Wilmington, Delaware 19899. Leaflet 800-4, 7/71, 10M, 47139H.
2. Davidson, R.L., Water soluble resins. New York 1962

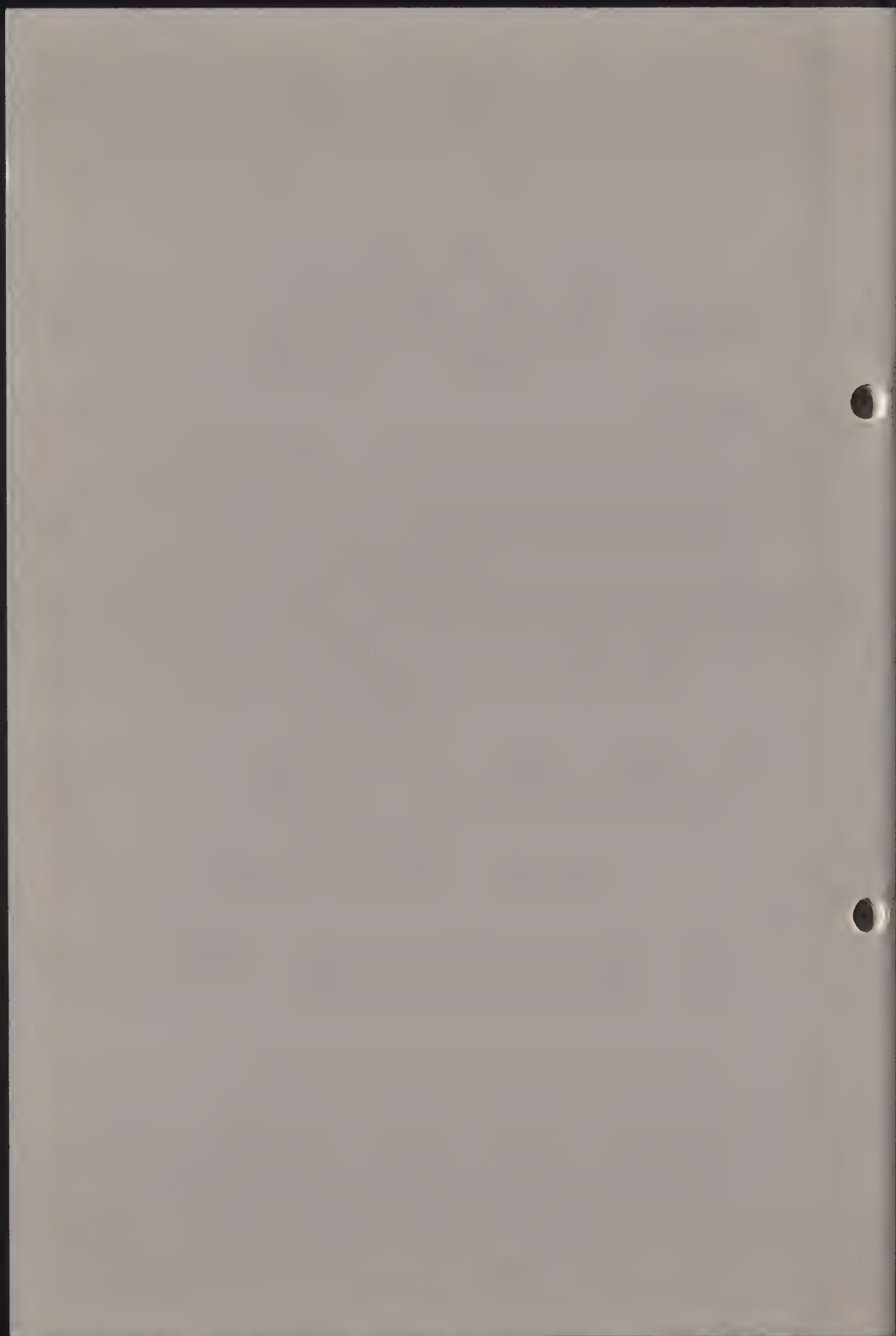


ASPECTS OF IMAGE SAFETY IN THE USE OF
ENZYMES IN PAPER CONSERVATION

Helen D. Burgess and Carmen L. Charette

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



ASPECTS OF IMAGE SAFETY IN THE USE OF ENZYMES IN PAPER CONSERVATION

Helen D. Burgess and Carmen L. Charette

Conservation Processes Research
Canadian Conservation Institute
Ottawa, Ontario K1A 0M8
Canada

ABSTRACT

Some aspects of image safety in the use of enzymes in paper conservation are considered. The effects of α -amylase and protease enzymes on the binding media (watercolour, gouache, casein, egg tempera and acrylic) were investigated along with writing and printing inks. The binding media study was performed on contemporary material while the inks were of historic origin. Treatments included both aqueous and partially non-aqueous (45% 2-methoxyethanol) systems.

1. INTRODUCTION

The enzymes that have found most use in paper conservation are α -amylases and proteases. These enzymes are now used for the release of backings, and for the removal of adhesive residues and sizes. Aqueous and partially non-aqueous systems have been successfully used (1, 2, 3) and the characterization of some of these proteins have been completed giving conservators more information on the conditions required for maximum efficiency (4).

In addition to the need for information on treatment conditions, it is vital to approach the question of whether enzyme processes have a detrimental effect on the artifact itself. Deleterious effects could take the form of deterioration of the support (i.e. the paper) or of the image. Materials in paper artifacts such as sizes, cellulose, gums, inks, pigments, binding media etc. could be affected by enzyme solutions. This study concentrates on the problem of safety of the image. Colour degradation by enzymes has been reported in the microbiological literature (5). However, there has not been any systematic study of the possible ill-effects of enzyme treatments on the image of an artifact.

The nature of many of the materials used in the preparation of artists' colours or inks suggests the possibility

of alteration due to enzyme action. If the binding medium contains starch or proteinaceous substances, damage could be caused by the use of α -amylases (which hydrolyze α -1,4-glucosidic linkages) and proteases (which hydrolyze peptide bonds in proteins), both of which are used by conservators. Enzymatic action on the components of the image may not be the only possible cause of damage. Since these proteins could act as wetting agents, as suggested by a previous study on permeation (4), surface action could also be important. Possible softening and losses of the image materials caused by surfactancy is thus considered.

The purpose of this paper is therefore to investigate some of the safety aspects relating to the binding media of materials such as artists' colours (watercolour, gouache, egg tempera, casein, acrylic) and inks. For the artists' colours study, only one pigment was used, phthalocyanine blue, because of its stability (6) eliminating the possibility of having the pigment affected by the enzymes rather than the binding medium. The colour change in the experimental samples may therefore be ascribed to an actual loss in pigment and not to a possible change in hue. Because of the unavailability of historic samples for artists' colours, samples prepared in the laboratory had to be used. By preparing uniform experimental samples, it was possible to semi-quantify colour changes caused by enzyme treatments.

The colour of an object can be specified by its tristimulus value (x, y, z) which represents the amounts of the three primary lights (red, green, blue) required to match the light of a specified wavelength. By measuring the tristimulus values of a naturally aged sample before and after treatment, the colour difference (ΔE) can be calculated using the CIE 1976 (L^*a^*b) colour difference formulae or CIELAB (7). Changes in colour can only be considered significant when ΔE is greater than 1.0 which is here considered as being the lowest perceptible value (8). Colour differences cannot be measured in the same way for ink samples which are of historic origin, because the inks do not cover a sufficient area to allow tristimulus value measurements. Therefore, the losses in colour have to be visually evaluated.

All the samples used in this study were coated on one side with starch or a proteinaceous adhesive which would be present in historic artifacts to be treated with α -amylase or protease when backings have to be removed. Enzyme treatments of samples included immersion in both aqueous (buffered and unbuffered) and non-aqueous (45% 2-methoxyethanol) systems. Enzyme performance is greatly dependent upon the pH of the solution. Experiments investigating the degree to which the addition of buffers to enzyme solution is necessary indicated that protease baths must always be buffered but that α -amylase treatments may be carried out without the

addition of a buffer, providing that the inherent acidity of the artifact is sufficient to bring the pH of the bath down to close to pH 5.0.

II EXPERIMENTAL METHODS

2.1 Preparation of samples of artists' colours

The paper used for the experiments was Arches Watercolour Paper, 140 lbs wt, hot pressed, smooth surface, 100% cotton. A paper of sufficient dimension to accommodate all binding media was soaked in water for approximately half an hour, stretched on a piece of plywood, and then fixed with tape. It was left to dry for one hour.

Five different binding media were used with the same pigment (phthalocyanine blue).*

1. Winsor and Newton Watercolour: Winsor Blue
2. Winsor and Newton Designer's Gouache: Winsor Blue
3. Winsor and Newton Artist's Acrylic colour: Winsor Blue
4. Shiva Casein colours Shiva Blue Deep (Phtalo)
5. Rowney Artists' Egg Tempera: Monestial Blue

The colour was applied as an even wash with a watercolour brush over the entire prepared sheet. Usually, a second wash of colour was applied after the first coat had partially dried.

After removing the paper from the board, a coat of either starch paste (20 g of wheat starch in 50 ml of water added to 175 ml of boiling water) or Nacan 18-8165 animal glue was brushed on the back of the sheet. The sheets were stored in a drawer for four weeks and then cut into 6.5 x 6.5 cm samples. Some samples were stored for eight and twelve weeks for additional testings.

2.2 Colour Difference Measurement

The tristimulus values (x, y, z) were measured for each sample of the different binding media before and after treatment (see section 2.3 for description of treatment). The tristimulus values were determined using a Hunterlab Colour Difference Meter Model D25D3 with a type A optical Sensor. The colour change (ΔE) was calculated using the CIE 1976 (L^*a^*b) colour difference formulae or CIELAB. Measurements of colour were taken in such a way as to minimize the

* Watercolour, gouache and egg tempera were analyzed by Neil Adair of the Analytical Research services CCI using x-ray energy spectrometry and x-ray diffraction, and were found to contain phthalocyanine blue. Manufacturer's literature indicated that the other colours (casein and acrylic) also contained phthalocyanine blue as a pigment.

error in readings, which means that each sample was placed in the same position for measurements before and after treatment. Measurements of colour for a series of samples were done to ensure that these measurements were reproducible (error less than 1%). The samples were kept flat during the reading by placing them between two thin glass plates.

2.3 ENZYME TREATMENT OF THE SAMPLES OF Artists' colours

The samples were treated individually, face-up, at 35°C for half an hour in the various baths described below. After treatment, the samples were rinsed for a few minutes in distilled water or in the solvent mixture. Each treatment was repeated three times or more, until the results were consistent. The colour difference value was calculated from an average of the three determinations. If the colour difference was significant for the samples aged for 4 weeks, the experiments were repeated with new samples that had been aged for 8 and 12 weeks respectively in order to ensure that colour loss was not due to the freshness of the samples.

When a sample was taken out of a bath, it was tested for softening of the colour by pressing a piece of white blotting paper on a corner of the sample. For those which transferred colour, a whole new sample was treated in exactly the same way as the sample partially blotted however, removal from the bath was followed by blotting of the whole surface. Tristimulus values of the blotting paper before and after treatment were taken and the colour difference calculated. This is an increase rather than a decrease in colour.

Description of the various baths used for treatments:

- Baths for samples backed with animal glue:

1st bath: Distilled water (100 ml)

2nd bath: Protease* (4 mg or 32 units) in distilled water (100 ml)

3rd bath: Protease (4 mg or 32 units) in pH 7.5 phosphate buffer (10 ml) + distilled water (90 ml)

4th bath: 2-methoxyethanol (45 ml) + distilled water (45 ml) + pH 7.5 phosphate buffer (10 ml)

* Enzymes used: The following enzymes are available from the Sigma Chemical Co., P.O. Box 14508, St-Louis, Missouri 63178, U.S.A.

1-Protease type I, pancreatic (bovine) crude P 4630

activity: 8 units/mg of solid.

one unit defined as the amount which will hydrolyze casein to produce colour (as per Folin-Ciocalteu reagent) equivalent to 1 μ mole tyrosine (181 μ g) per minute at pH 7.5 and 37°C. (3)

pH optimum: ~7.5 (3)

5th bath: Protease (4 mg or 32 units) in 2-methoxyethanol (45 ml) + distilled water (45 ml) + pH 7.5 phosphate buffer (10 ml)
 protease stock solution: 40 mg (320 units) of protease is dissolved in 10 ml of pH 7.5 phosphate buffer and 1 ml (4 mg) of this solution used for the treatments.

- Baths for samples backed with starch:

1st bath: distilled water (100 ml)

2nd bath: α -amylase* (0.1 g or 3600 units) in distilled water (100 ml)

3rd bath: α -methoxyethanol (45 ml) + distilled water (45 ml) + pH 5.0 acetate buffer (10 ml)

4th bath: α -amylase (0.1 g or 1200 units) in 2-methoxyethanol (45 ml) + distilled water (45 ml) + pH 5.0 acetate buffer (10 ml).

- The buffer solutions were prepared according to the following procedure:

1) 0.20M sodium phosphate:

$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ (31.2 g) was dissolved in distilled water (800 ml) and 5% NaOH (~125 ml) added to produce a pH of 7.5.** The volume was adjusted to 1. liter.

2) 0.10M sodium acetate:

Glacial acetic acid (6 ml) was added to distilled water (800 ml) and 5% NaOH (~60 ml) added to produce a pH of 5.0. The volume was adjusted to 1.0 liter.

Both buffer solutions were stored in the cold at 1 to 3°C. The phosphate buffer may be kept for one month but the acetate buffer should be made up fresh every week.

2.4 Sensitivity of Inks to Enzyme Treatment

A variety of examples of writing and printing inks was

* 2. α -amylase: type X-A: Fungal crude from Aspergillus oryzae, A 0273

Activity: 36 units/mg of solid

one unit defined as the amount which will hydrolyze 1.0 mg of maltose from starch at pH 6. at 20°C (9)

pH optimum: ~5.0 (3, 10)

It has been shown that the activity of these enzymes is decreased in 45% 2-methoxyethanol (2). The activity for the α -amylase in the solvent mixture was determined as being three times lower than that in the aqueous system. No difference in the results was obtained by increasing enzyme concentrations to compensate for the lower activity.

** The pH was determined using a standard glass electrode with a Fisher Accumet 420 pH meter, calibrated by Fisher Scientific Company certified buffer solutions at pH 4 and 7 where appropriate.

spot-tested for stability in the aqueous system. If no loss was observed, the sample was treated with the aqueous enzyme (α -amylase or protease) solution; if the ink proved to be sensitive to water, it was spot-tested with the partially non-aqueous (45% 2-methoxyethanol) system. Those stable in this medium were then treated with the enzyme solutions. The samples to be treated in a protease bath had been coated on one side with the animal glue while those for the α -amylase treatments had been coated with starch paste, as with the samples for the study of artists' colours. The conditions for enzyme treatment were also the same as those used for the artists' colours study.

III RESULTS AND DISCUSSION

3.1 Effect of protease on artists' colours

The results for the glue backed samples of the various media are shown in Table 1.

Table 1: Colour difference (ΔE) of glue backed samples treated with protease in aqueous or partially non-aqueous (45% 2-methoxyethanol) system at 35°C for 30 minutes.

Binding Medium	Treatment baths				
	H ₂ O	H ₂ O + protease (32 units or 4 mg)	H ₂ O + pH 7.5 buffer + protease (32 units or 4 mg)	45% 2-methoxy-ethanol	45% 2-methoxy-ethanol + protease (4 mg)
Casein	N.L.	N.L.	N.L.	N.L.	N.L.
Acrylic	N.L.	N.L.	N.L.	N.L.	N.L.
Gouache	N.L.	2.6	2.8	N.L.	N.L.
Egg Tempera	N.L.	N.L.	1.2	N.L.	N.L.
Water-colour	N.L.	1.2	1.4	N.L.	N.L.

N.L.: no loss

Losses were observed for gouache, egg tempera and watercolour; the changes for the last two are considered to be at the lower limit of detectability for the human eye and as being very minor losses. There was little difference between the buffered and unbuffered treatments and, since the buffered bath may be expected to have about 1.5 times

the activity of the unbuffered solution (3) (assuming constant concentration), it is therefore likely that enzymatic cleavage of some constituent of the binding media is not the only factor causing the observed pigment loss. The gouache samples, naturally aged for 8 and 12 weeks, gave similar results when treated.

The relatively small changes observed in the protease treatments may possibly be related to a slight solubility or softening of the colours in the two solvent systems. The enzyme itself may be acting as a surfactant and thus aid in a swelling of the binding medium resulting in a subsequent loss of pigment. There was no evidence of protein material in an i.r. spectroscopic analysis (detection limit: 5% of protein) of the binding media of the gouache or watercolour*, nor was there any mention of proteinaceous substances being included in the preparation of those materials in the literature. It is surprising that the casein and egg tempera (protein containing) samples lose such a little quantity of pigment when treated with protease. This could be caused by a smaller degree of swelling of these substrates during treatment.

The results in Table 2 show that both water and the partially non-aqueous (45% 2-methoxyethanol) system are capable of softening the gouache and watercolour samples which are backed with animal glue. There was no softening of the other binding media samples (acrylic, casein, egg tempera).

Table 2: Colour transfer (ΔE) obtained by pressing a blotting paper on glue backed samples treated with protease in aqueous or partially non-aqueous (45% 2-methoxyethanol) system.

Binding Medium	Treatment baths			
	H ₂ O	H ₂ O + pH 7.5 buffer + protease (32 units or 4 mg)	45% 2-methoxy-ethanol	45% 2-methoxy-ethanol + protease (4 mg)
Gouache	1.6	4.9	1.5	1.8
Water-Colour	2.1	2.2	1.2	2.2

Only the loss during the buffered protease treatment of gouache samples is significantly larger than the solvent

* Analysis of the binding media was carried out by Elizabeth Moffatt of the Analytical Research services, CCI. Gum arabic was identified as a constituent for both the gouache and watercolour colours.

controls. Because of the difficulty in standardizing the pressure, transfer observations are not as reliable as the direct colour loss measurement. Transfer observations do however indicate that gouache and watercolour are more likely to be softened during treatment than are the other media.

Casein and egg tempera do not swell as much as gouache and watercolour during treatment and are thus quite insensitive to baths containing protease.

3.2 Effect of α -Amylase on Artists' Colours.

The results for samples backed with starch are given in Table 3.

Table 3: Colour difference (ΔE) of starch backed samples treated with α -amylase in aqueous or partially non-aqueous (45% 2-methoxyethanol) system at 35°C for 30 minutes.

Binding Medium	Treatment baths			
	H ₂ O	H ₂ O+ α -amylase (3600 units or 0.1 g)	45% 2-methoxy-ethanol	45% 2-methoxy-ethanol + α -amylase (0.1 g)
Casein	N.L.	4.7 (4weeks) N.L. (8weeks)	N.L.	N.L.
Acrylic	N.L.	N.L.	N.L.	N.L.
Gouache	N.L.	5.1 (4,8,12weeks)	N.L.	N.L.
Egg Tempera	N.L.	N.L.	N.L.	N.L.
Water-Colour	N.L.	N.L.	N.L.	N.L.
N.L.: no loss				

Only the casein and gouache samples treated in the aqueous enzyme bath showed colour losses at four weeks after sample preparation. After 8 and 12 weeks of natural aging, only gouache was still losing colour indicating that the sensitivity of the casein was a transitory phenomenon which was probably related to the young age of the colour samples.

Table 4: Colour transfer (ΔE) obtained by pressing a blotting paper on starch backed samples treated with α -amylase in aqueous or partially non-aqueous (45% 2-methoxyethanol) system.

Binding Medium	Treatment baths			
	H ₂ O	H ₂ O + α -amylase (3600 units or 0.1 g)	45% 2-methoxyethanol	45% 2-methoxyethanol + α -amylase (0.1 g)
Gouache	N.T.	2.5	N.T.	N.T.
Water-colour	1.3	2.6	1.1	N.T.
N.T.: no transfer				

Table 4 shows the colour transfer data for the 4 week old starch backed samples. Only gouache and watercolour samples showed transfer of colour. Trace levels were observed for watercolour samples treated with solvent alone (water or 45% 2-methoxyethanol) but the enzyme immersion resulted in more significant colour softening for both gouache and watercolour.

Minor softening may be explained either by the comparative freshness of the colour and/or by a surface activity relating to the physical nature of the protein itself. This phenomenon was investigated using starch backed gouache samples as a substrate for the α -amylase, Lissapol NDB and casein (see Table 5).

Table 5: Colour difference (ΔE) for gouache starch backed samples treated with Lissapol NDB, casein or α -amylase in aqueous and partially non-aqueous (45% 2-methoxyethanol) systems for investigation on enzyme surfactancy properties.

	H ₂ O	45% 2-methoxyethanol
Solvent alone	N.L.	N.L.
Solvent + Lissapol (0.1% v/v)	1.2	N.L.
Solvent + casein (0.6 g)	1.2	N.L.
Solvent + α -amylase (3600 units or 0.1 g)	5.1	N.L.
N.L.: no loss		

No loss was observed in any of the 2-methoxyethanol treatments, probably because the reduced swelling of substrate in this solvent makes the colour less susceptible to the surfactancy of Lissapol NDB, casein or α -amylase. However, in the water bath (where considerable swelling of the substrate may be expected), the Lissapol NDB and casein possess approximately equal surface action.

The α -amylase treatment of gouache results in considerably more loss than the Lissapol and casein indicating that the change in colour is not only caused by the protein acting as a surfactant. It was found that the gouache used in this case contained a 4:1 ratio of dextrin to gum arabic (11). α -Amylase is specific for the α 1,4-glucosidic linkage. It hydrolyses starch and the residual polysaccharide of starch (dextrins) to give maltose and eventually glucose. The watercolour used in these experiments does not contain any dextrin or starch but only gum arabic which would not be attacked by α -amylase. Therefore, the hydrolytic action of the amylase upon the dextrin is the cause of much of the colour loss in the gouache samples.

In order to investigate the possibility that the magnitude of the ΔE values was a function of the density of the pigment wash, samples made up with a lighter (less dense) wash were treated as previously described with α -amylase. They experienced less colour loss ($\Delta E \sim 1.2$) compared to the more dense coat ($\Delta E \sim 5.1$). This demonstrates the greater vulnerability of the thicker wash, probably due to greater availability of the pigment to the solvent media. Similar observations were obtained with protease treatments.

The effect of enzyme concentration on colour loss for gouache samples was studied by treating samples naturally aged for 12 weeks in aqueous solutions of various enzyme concentrations (36, 72, or 108 units/ml). Treatment conditions were the same as those described earlier. Similar ΔE values of 5.0, 4.8 and 5.1 were obtained indicating that the rate of colour loss is not dependent on the rate of enzyme action on substrate (as concentration of enzyme goes up, the rate of reaction would be expected to increase) but on the accessibility of the colour substrates to enzyme. Physical interactions including surfactancy are thus very important to the changes of samples during enzyme treatment.

3.3 Effect of enzymes (α -amylase and protease) on writing and printing inks

A list of the various inks treated with enzymes is given below. Providing that the ink was not sensitive to the solvent being used, it was not possible to see any loss in density in any of the samples due to enzymatic action. With the limited sample size, it is difficult to be conclusive but the evidence is that α -amylase and protease enzymes pose little or no problem to the security of inks. Binding

media in inks are usually mixtures of various gums and drying oils which should not be hydrolyzed by α -amylases or proteases.

A - Inks treated with α -amylase and protease in aqueous systems.

1. Writing inks

Ledgers:

1905 (black)
c1920 (black)
1957 (blue ballpoint)
1963 (blue and black ballpoint)
1964 (blue and black ballpoint)
1881 (black, brown and blue)
1883 (brown)
1886 (blue-black)
1905 (black) receipt

Autograph book:

Miscellaneous:

2. Printing inks

Newsprint (black):

1867 scrapbook
late 19th century scrapbook
c1920 scrapbook

Magazines

illustrations (black):

c1880
1883

Receipts:

1905 (black, pink and blue)
c1910 (black, pink and blue)

Chromolithographs:

c1860 (black, red, yellow, blue,
and gold)
1865 (green, red, yellow,
and black)
c1865 (red, green, blue, brown
and black)
c1865 (black, silver and gold)
c1865 (green, blue, yellow
and red)
1881 (blue, yellow, brown
and red)

B - Inks treated with α -amylase and protease in partially non-aqueous systems (45% 2-methoxyethanol).

Autograph book:

1881 (black writing ink, 3 examples)
1883 (black writing ink)

Ledgers:

1880 (black writing ink)
1882 (black writing ink)
1965 (black ballpoint ink)

IV SUMMARY

The results presented in this paper are a preliminary survey of some of the possible effects of enzymes on the safety of the image of artifacts.

This study would suggest that binding media (gouache,

watercolour, acrylic, casein, egg tempera) appear to be safe when experimental samples are treated with enzymes (α -amylase and protease). However, it should be emphasized that the samples used were experimentally produced and the pigment chosen (phthalocyanine blue) was known to be stable. Historic samples and other pigments, dyes, etc would not necessarily behave in the same way. Careful note should also be taken of the following considerations when using enzymes systems.

1. Enzymes may contribute to softening and loss of colour by acting as surfactants during treatment. This effect may diminish as the age of media increases and becomes less subject to swelling.
2. The presence of dextrin or starch, or proteinaceous material in the image layer could make it susceptible to the action of α -amylase or protease respectively.
3. The partially non-aqueous (2-methoxyethanol) enzyme baths have less detrimental effects on image colour than the aqueous treatments.
4. α -amylase and protease have few ill-effects on writing and printing inks.

There are other situations where the image could be affected by enzymes (α -amylase and protease) which have not been discussed in this study. Proteases could attack the image of paper artifacts containing distemper pigments (animal glue as medium) in much the same way as the α -amylase acted upon the gouache containing dextrin. Another difficulty may arise from enzyme treatment of coated papers that contain substantial amounts of starch or casein. Loss of image may result if an α -amylase or protease was able to attack the paper coating. These and other problems will be addressed in this continuing study.

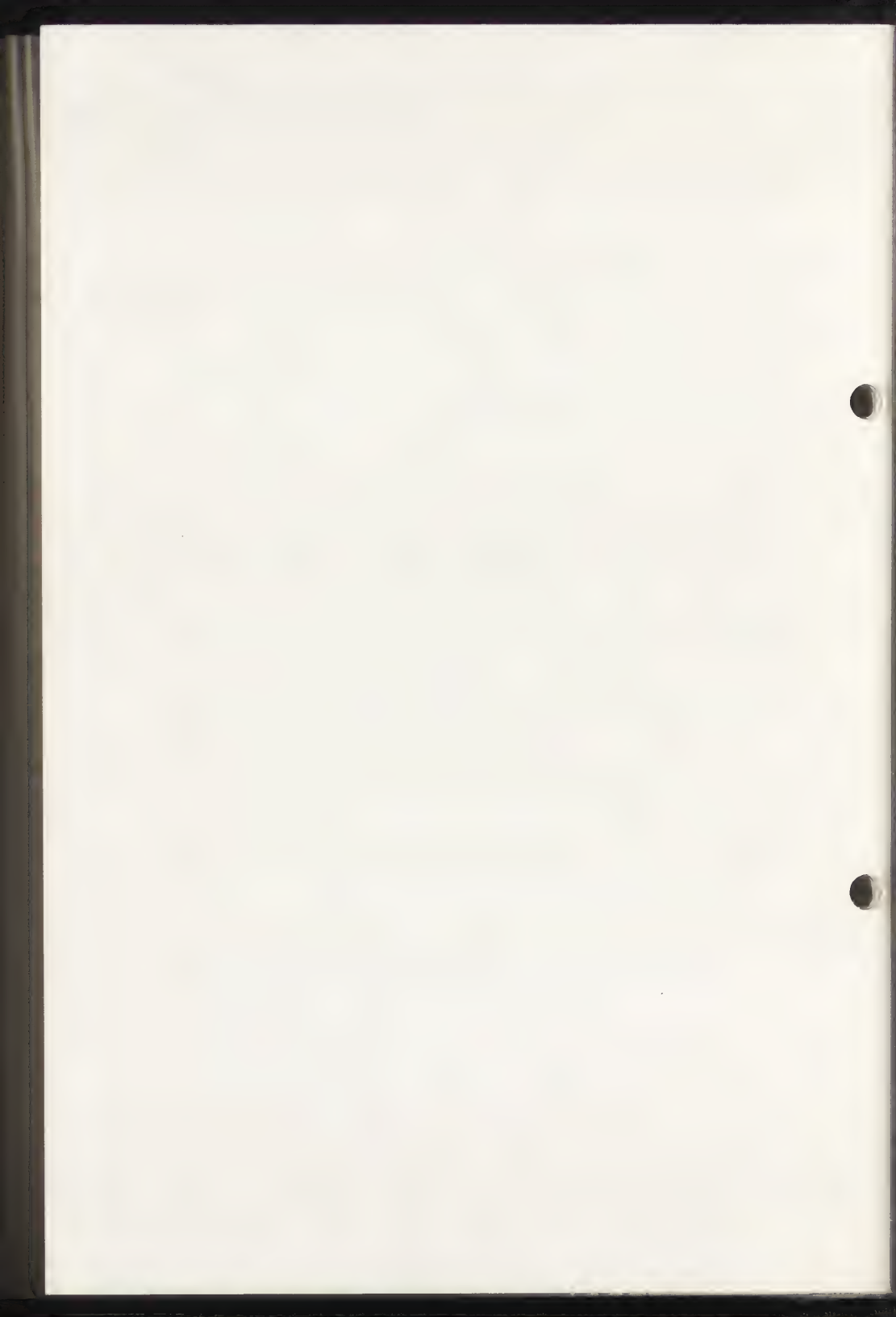
Acknowledgements

The authors are grateful to David W. Grattan, Conservation Processes Research CCI, for his assistance in the planning of this project. We would also like to thank J. Clifford McCawley, Chief, Conservation Processes Research CCI for his helpful comments during both the project and the preparation of this paper.

References

- (1) Segal, J. and Cooper D, "The Use of Enzymes to Release Adhesives", The Paper Conservator, Vol. 2, 1977, pp. 47-51.
- (2) Cooper, David, Carolyn King and Judith Segal, "The Use of Enzymes in Partially Non-aqueous Media", The Conservation of Library and Archive Materials and the Graphic Arts, Proceedings of the Cambridge 1980 Conference, 1981 (in press).

- (3) Van Oort, Willem P. and Peter M. Poldervaart, "Prints off The Ice: The Conservation and Restoration of the Nova Zembla Prints", see reference (2).
- (4) Grattan, David W., Johanne St-Hilaire, Helen D. Burgess and J. Clifford McCawley, "The Characterization of Enzymes for Use in Paper Conservation", see reference (2).
- (5) Dholakia, J. N. and H.S. Chhatpar, "Control of Some Fungi Capable of Degrading Cellulose and also Water Based Poster Colours", International Biodeterioration Bulletin, spring 1980, pp. 17-21
- (6) Gettens, Rutherford J. and George L. Stout, "Painting Materials: A Short Encyclopedia" (New York: Dover Publications Inc, 1966), p. 137.
- (7) Robertson, Alan R., "The CIE 1976 Color-Difference Formulae," Color Research and Application, Vol. 2, no.1, spring 1977, pp. 7-11.
- (8) Personal communication with Alan R. Robertson, Division of Physics, National Research Council of Canada, Ottawa, Ontario.
- (9) Bernfield, P., "Methods in Enzymology", Vol. 1, (New York: Academic Press Publisher, 1955), pp. 149-150.
- (10) Wiseman, Alan, "Handbook of Enzyme Biotechnology", (New York: Ellis Horwood, 1975), p. 135.
- (11) Personal communication with Peter Staples, Technical Director at Winsor and Newton, Wealdstone, Harrow, England.



81/14/11

BIOLOGICAL METHODS IN BOOK RESTORATION

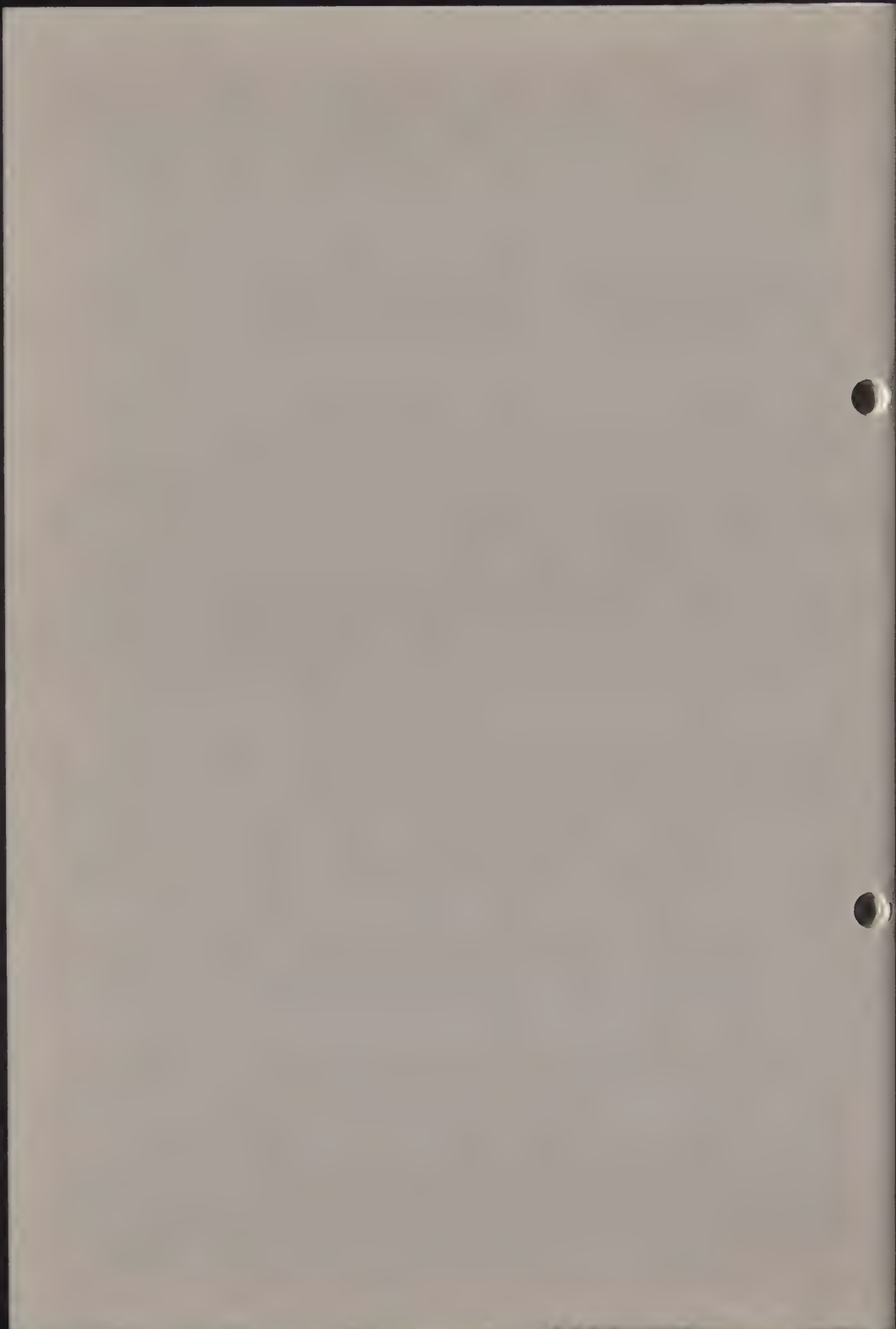
Ju. P. Nyuksha

ICOM Committee for Conservation

6th Triennial Meeting

Ottawa 1981

Working Group: Graphic and Photographic
Documents



BIOLOGICAL METHODS IN BOOK RESTORATION

Ju. P. Nyuksha

Chief of the Book Conservation and Restoration Department
M.E.Saltykov-Shchedrin State Public Library
Sadovaya 18
191069 Leningrad
USSR

The scientific level of restoration is dependent on the accuracy of reactions used to reach the effect. Chemical reactions are less accurate than biological ones. The latter are of high specificity. They provide strict trend action on any of the object components. Biological reactions permitted to obtain high effectiveness of restoration. Use of proteases, amylases and cellulases leads to results unavailable to other working methods. Experiments with amylolytic ferments allowed explanation of the processes occurring during cleaning of the materials being restored to get rid of products harmful in subsequent conservation. The processes are characterized by the accumulation of maltose in working solutions. It has been proved that increasing ferment concentration does not contribute to corresponding increase in biochemical reactions. The most effective reactions occur for concentrations up to 1%. Subsequently, the process slows down. Book restoration is suppressed especially if starch is found between paper layers. Rapid exhaustion of solutions can be explained by ferment accumulation in paper. Various ferment preparations can be used in restoration work. Proteases and lipases contribute to cleaning of dirt accumulated in long-term use. Cellulases and proteases sensibilise a document to repairing with synthetic

polymers. Investigation into the possibilities of cleaning various kinds of paper of organic dirt, completely harmless for the book, are given.

The main objective of scientific restoration is to treat one component of the original leaving all of its other parts unaffected. This is especially important during de-restoration and also in cleaning a document of various substances which have served their time and which formed again as the result of ageing.

It has been known that in biological objects, a number of complicated reactions are fully provided by ferments. They are biological catalyzers of protein origin. Ferments are distinguished by their specific activity with respect to other substances.

The substances on which ferments act and which are activated by them are called substrates. Substances which do not take part in reaction but which slow down the rate of fermentation conversions are called inhibitors. Every ferment most often accelerates only one biochemical reaction. Taken together, all ferments have an extremely wide spectrum of action. Ferments have left the sphere of intercellular biochemistry. They are accumulated in great amounts, cleaned, concentrated in the form of ferment preparations and are used for practical purposes in industry, agriculture, and medicine.

Use of ferment preparations increases immeasurably the accuracy and effectiveness of many technological processes. This also wholly applies to work in the field of restoration of cultural values. It has been established with certainty that fermentive reactions are useful for the restoration of printed works and manuscripts. Two most important features of fermentive reactions are successfully used: specificity and great acceleration of reaction. Practical application of these specific catalyzers requires certain knowledge of their properties [1-3]. The surface of any protein, including a ferment

protein, is a mosaic of various chemical groups belonging to the side-chains of aminoacids. Unique specificity is determined by the relatively strict arrangement of a multitude of heterogeneous functional groups in a molecule.

A molecule of the ferment protein, which combines directly with substrate and on which depends the catalytic activity, is called the active centre. This is a complicated structure adapted for close connivention and interaction with a substrate molecule and oriented attachment. This provides a high degree of affinity in the formation of an intermediate complex of the substrate and catalyzer with a great statistical probability.

Ferments function most successively in aqueous media. For disorganized motion of the molecules in solutions, the probability of usual reaction, in practice, is determined by the concentration of substances. The reactions, hardly probable for small concentrations, become highly effective using fermentation catalysis.

Fermentive reactions occur only in strictly definite conditions. The first of these is an appropriate substrate. For relatively small amounts of it the rate of the process is directly dependent on concentration. Substrate excess often leads to reaction inhibition. The products of hydrolysis of complex molecules themselves turn into the substrate. This is equivalent to an increase in its concentration and leads to a reduction in fermentive activity.

Different chemical substances stimulate or inhibit ferment activity quite individually. Ethyl alcohol, acetone and other organic solvents denature ferments. Antiseptics can deactivate them. The salts of heavy metals, in particular, silver, mercury and copper are especially poisonous.

Ferment activity increases at temperatures of about 40° . Low, above-zero temperatures inhibit their action. At a temperature exceeding $45-60^{\circ}\text{C}$ ferments are inactivated. Optimum temperature for ferments extracted from

animal tissues varies within 37-40° and for those extracted from plants and microbes, from 32 to 60°C. The degree of catalytic effect of every ferment is affected by optimum pH value within a narrow limit. Its alteration leads to a reduction in the effectiveness very strongly. Most ferments have a pH optimum within 4-8. At pH below 5 and above 9, many ferments are inactivated. For realising fermentive reactions, use is made of buffer solutions. Other features can be considered in connection with the designation of individual fermentive preparations.

THE PROTEASES. Proteolytic ferments catalyze protein decomposition reactions and the products of protein desintegration. Hydrolytic decomposition of the peptide linkage -CO-NH- is given by the sequence of the following reaction



This yields peptone and free amino acids.

The proteases are subdivided into peptidases and proteinases [4_/. The peptidases break down only the peptide linkages which set in conjugation the end residues of amino acids with the main peptide linkage. The conjugated proteinases break down proteins according to linkages which are inside the polypeptide chains. Ferments of this kind can be acidic (pH optimum = 2.5-6), alkaline (pH optimum = 7.7-10) and neutral (pH optimum = 7.0-7.5). The latter hydrolyze casein, gelatin and egg albumin most actively. Thus, medium reaction and substrate specificity both make neutral proteinases more beneficial for the purposes of restoration than others.

Proteases can be of animal and plant origin. Plant proteases are obtained from parts of plants and from fungi and bacteria. Ferments are sensitive to the presence of some anti-fungal substances. The activity of proteinase *Asporyzae* increases in the presence of $(\text{NH}_4)_2 \text{SO}_4$ and NaCl [5_/. Keratin, the wool protein, is put to hydro-

lysis by the proteolytic ferments of actinomycetes.

A study of ferments reveals their multicomponent nature. Thus, a most effective proteolytic ferment of the pronasa type consists, according to some data, of 14 components of different specific action, and this is what determines its high effectiveness /6_/. .

THE CARBOHYDRASES catalyze the hydrolysis and synthesis of glucosides and di-, tri- and other polysaccharides; hydrolysis is directed towards the linkage $-C - O - C -$. This ferment saccharifies starch by 98-99%, glycogen by 90%, decomposes saccharose and inulin. Amylase effects hydrolysis of the α -1.4 glucan linkage of starch and glycogen with formation of dextrans and maltose / 7_/. .

Starch hydrolysis by amylases is revealed in different ways: (1) liquefaction, a decrease in viscosity with solution; (2) dextrinizing, decomposition with a change in iodine reaction: from blue to colourless through violet, cherry-red, red-brown, brown-yellow, and light-yellow; (3) saccharifying down to maltose, completely or partially. The ferments causing these processes are subdivided accordingly. α -amylases - dextrinases occur nearly always in combination with β -amylases. β -amylases often occur separately, without α -amylases. Both are incapable separately of completely catalyzing the hydrolysis of starch and glycogen. In the case of their simultaneous action, starch is hydrolyzed by 95%.

Among ferments acting on fats and oils, lipase is the one most thoroughly studied. Its action is directed towards the complex ether linkage-bonded glycerine and high-molecular fatty acids. In an aqueous medium lipases lose their activity very rapidly. They are much more stable in glycerine medium.

Fermentation catalysis is used successfully in restoration work for changing or extracting separate

component parts of the material to improve it or to give it properties necessary for future work /8/. Using historical evidence about a document, its constituent materials and methods of previous restoration, it is possible to fix upon fermentive reactions for every work.

The present crude products are complexes of different ferments of single-substrate action, sometimes with an admixture of other ferments. In order to preserve a document being conserved, it is necessary to know all the active components of the preparation.

Ferment preparations are used in the form of aqueous solutions. They are prepared using clean glass or enameled ware and chemically pure reagents. Dissolution in buffer mixtures provides a permanent pH level during the entire process of treatment. Use of a phosphate buffer providing a pH from 5.8 to 8 is favourable and harmless for book paper. Mixing and pouring is done by hand without using mechanical mixers to avoid foam formation which inactivates ferment proteins.

The simplest case of application of ferment preparations is the removal of protein and starch adhesives from cellulose material. These substances are decomposed or transferred chemically with time. Consequently, they lose their bonding properties and become contaminants adversely affecting subsequent conservation. They also prevent realisation of conservation and restoration using synthetic and artificial polymers. To remove them, use is made of proteases and amylases.

In the case of fermentation hydrolysis of protein-starch inclusions in paper the substrate is highly concentrated because it is arranged in a comparatively thick layer. Ferment influence upon the substrate is difficult. Accumulation of intermediate products leads to an increase in the concentration of substrates. Evidently, ferment action is directed, in the first place, towards the molecules which transferred to liquid phase, whereas the

molecules attached to fibres within the paper remain intact for a long time. Different kinds of starch and starch grains themselves are heterogeneous. They consist of amylose and amylopectin. The former hydrolyzes more easily and the latter, with more difficulty. Original starch grains are much less accessible to ferments than the ones decomposed due to heating during the making of paper. In this case, amylose is freed of amylopectin and is readily fermented by beta-amylase. Starch obtained from different plants reveals an unequal amylose-to-amylopectin ratio. There is little amylose in rice starch, somewhat more in corn and potato starch and still a greater amount in wheat starch. It is just in this sequence that susceptibility of these kinds of starch to fermentation hydrolysis increases.

Use of amylases for the purpose of de-restoration of library stocks has yielded good results. Any kind of patches and impregnation compounds of flour and starch adhesive can be completely removed without mechanical effort during 10-15 min.

A study of the dynamics of this process is shown in Fig. 1. Hydrolysis of the starch by amylase *Bacillus subtilis* was determined using the accumulation of maltose in working solution. The criterium used was the coefficient (K), a relative quantity expressing the ratio:

$$\frac{\text{glue remaining in paper}}{\text{glue hydrolyzed by ferment}}$$

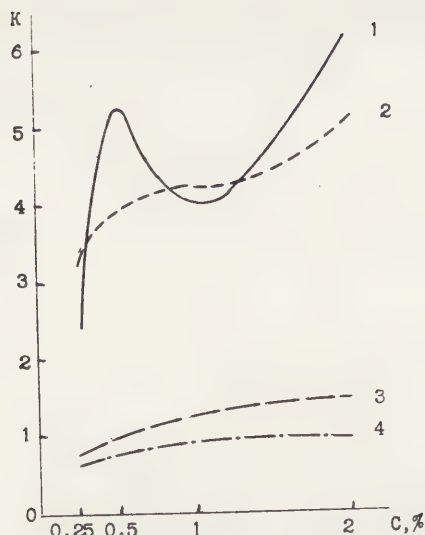


Fig. 1 Starch hydrolysis coefficient versus ferment concentration

- 1 - starch between sheets of paper,
 2 - same, after increased-temperature processing,
 3 - starch surface-coated paper,
 4 - same, after increased-temperature processing.
 The abscissa - concentration, %.
 The ordinate - coefficient.

Rapid increase in the rate of substrate hydrolysis occurred with increasing concentration of amylase to 1%. Further on, the process slowed down. Paper patches reduced its rate 5-6 times. Hydrolysis effectiveness invariably decreased with ageing of a document.

Fig. 2 shows a dependence of the coefficient on the length of hydrolysis. It is confirmed that starch in the adhesive contained between sheets of paper is hydrolyzed with difficulty. It was hydrolyzed during as long as 40-50 min, whereas for open adhesive films this required only 15-20 min.

In a solution of proteinases there occurs removal of animal glue from the backs of old books and separation of the sheets sticking due to softening of the surface gelatin and casein sizing.

During restoration of paper sheets it is important to free and loosen the edges of breaks. Action of proteases, amylases, cellulases (C_x -ferment which acts on cellulose derivatives), and some others yields excellent results. Ferments are known to give especially good strength of attachment of new and old paper in making the missing parts of sheets of paper pulp.

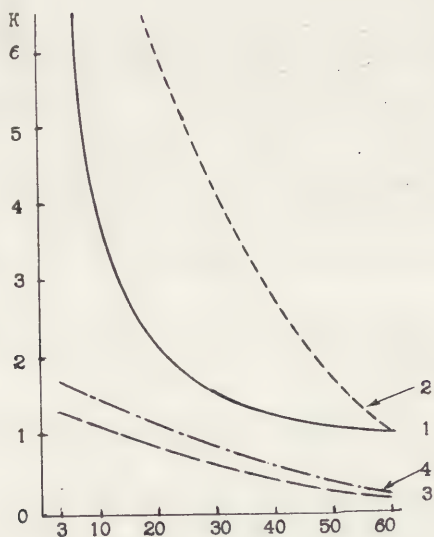


Fig. 2 Starch hydrolysis coefficient versus processing time

1, 2, 3, 4 - same as Fig. 1.

The abscissa - time, min.

The ordinate - coefficient.

The problem of removing old dirt, in particular, from the corners of used books is certainly a complicated one. This dirt is always non-homogeneous, has a mixed nature and changes its composition very strongly with time. Dirt is readily removed by treatment with proteinases and lipases.

Use of the polygalacturonase (pectinase) and lignin-destroying ferments for obtaining processed pulp, some cytolytic ferments for breaking down the fungi mycelium in paper, etc., appears to be quite promising.

The possibilities of using ferment preparations in restoration are not confined to the above-mentioned cases. In the course of development of microbiological industry and progress in the use of methods for the conservation of cultural values, the field of application of the fermentation catalysis will spread.

REFERENCE

1. Konovalov S.A. Biosintez fermentov mikroorganizmami. M., Pishchevaya promyshlennost, 1972, 270 p.
2. Rose A.H. Chemical microbiology. London, Butterworths, 1968, 312 p.
3. Bunker H.J. Fermentation advances /Ed. D. Perlman). New York, London, Academic press, 1969, 909 p.
4. Mosolov V.V. Proteoliticheskie fermenty. M., Nauka, 1971, 414 p.
5. Babakina V.G. Primenenie fermentov v proizvodstve kozhi. M., Rostkhimizdat, 1962, 240 p.
6. Petrova I.S. Proteoliticheskie fermenty aktinomitsvetov. M., Nauka, 1976, 60 p.
7. Pronin S.I. Amiloliticheskie fermenty i ikh rol v pishchevoy promyshlennosti. M., Gizlegpishchprom, 1953, 220 p.
8. Nyuksha Yu.P. Tekhnologicheskie protsessy restavratsii na osnove biologicheskii aktivnykh veshchestv. In: Teoria i praktika sokhraneniia knig v biblioteke. Gos. publ. b-ka im. M.E. Saltykova-Shchedrina. L., 1975, vyp. 7, p. 75-101.

THE ELIMINATION OF CHLORAMINE-T RESIDUES
THROUGH THE USE OF REDUCING AGENT
ANTI-CHLORS

Helen D. Burgess

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981.

Working Group: Graphic and Photographic
Documents



THE ELIMINATION OF CHLORAMINE-T RESIDUES THROUGH THE USE OF REDUCING AGENT ANTI-CHLORS

Helen D. Burgess

Conservation Processes Research
Canadian Conservation Institute
1030 Innes Road
Ottawa, Ontario K1A 0M8
Canada

Abstract

A comparative study of the ability of six different reducing agents (sodium borohydride, tetramethylammonium borohydride, tetraethylammonium borohydride, sodium sulfite, sodium thiosulfate or sodium hydrosulfite) to eliminate chloramine-T bleaching residues from paper has been completed. The investigation has been carried out as a function of anti-chlor concentration (0.1 to 2%) and solvent (water or alcohol). Evaluation of results took place after five months of natural ageing in the dark and showed the borohydrides to have similar abilities to successfully remove oxidizing residues. Treatment of bleached paper with the sulfur-based reducing agents showed evidence of incomplete removal of bleaching residues.

I. Introduction

The advantages of bleaching paper artifacts with chloramine-T (*i.e.* minimal effects on coloured dyes and pigments, relatively slow rate of fibre degradation, and an easily controlled end-point for the bleaching process) has been recognized by many conservators.¹ Recent work has demonstrated, however, that there is considerable difficulty in the complete removal of bleach residues^{2,3,4}: extensive washing of experimental papers for up to sixteen hours has not been sufficient to remove all traces of chloramine-T. The presence of aluminum in the paper fibres, usually in the form of alum, has been implicated as an important contributing factor^{3,4}. Another theory is that the ion-exchange capacity of the cellulose in paper is sufficient to strongly absorb, complex, and retain bleach residues². Both explanations have been investi-

gated and the first was concluded as being, by far, the most important.

Residual bleach in paper results in an increase in the brightness of the objects after several months' storage (*i.e.* the chloramine-T continues its bleaching action). This, plus the strong possibility that the fibres are being degraded during storage, has persuaded many conservators to use other systems for stain removal. An alternative may be to use an appropriate anti-chlor immediately after the chloramine-T treatment. The majority of anti-chlors for oxidizing bleaches like chloramine-T are reducing agents which can readily react with an oxidizing agent. The purpose of this study is to examine the ability of several of these reducing agent compounds (sodium salts of sulfite, dithionite and thio-sulfate; sodium borohydride and the tetramethylammonium and tetraethylammonium borohydride salts) to effectively stop the action of residual chloramine-T. It has also been possible to investigate the bleaching effects of the individual anti-chlors (during the treatment itself) as well as the degree of brightening of papers treated with specific chloramine-T: anti-chlor combinations. For these studies, the chloramine-T bleaching and the sulfur containing anti-chlor treatments were performed in aqueous media, while the borohydride processes were carried out using aqueous and non-aqueous procedures.

The brightening of papers during treatment and storage was measured by following the colour change of 19th century, yellowed paper samples by spectroscopic analysis (reflectance measurement) at 416 nm.

Chemistry of the Reducing Agents

Anti-chlors, which are reducing agents, react with bleaches (*i.e.* oxidizing agents) to yield an oxidized form of the anti-chlor and a reduced form of the bleach. The anti-chlor has gone to a higher oxidation state while the bleach has changed to a lower one. The tendency of this reaction to proceed will depend upon the oxidation potential of the system which is, in turn, a function of such parameters as pH, temperature, and the concentration of anti-chlor and bleach.

The reducing agents used in this study may be divided into two categories: borohydrides and sulphur containing compounds. The chemistry of both the sulfur⁵ and the borohydride^{6,7} compounds is well documented. The sulfur anti-chlors show little specificity and are able to react with all of the common chlorine bleaches (eg: hypochlorite, chloramine-T, chlorite and chlorine

dioxide) and hydrogen peroxide. They can also reduce and hence decolourize ferric (Fe^{+3}) compounds, some organic dyes, and other coloured species commonly associated with paper artifacts⁵.

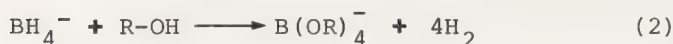
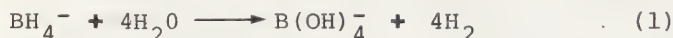
The sulfur anti-chlors are used dissolved in water and are stable enough for use in this form. The relative reducing power of these reagents is as follows:

thiosulfate > dithionite > sulfite

Sulfate is the final oxidation product in all cases.

In comparison to the sulfur compounds, the reducing powers of the borohydrides are far more extensive. In addition to the species mentioned above, they react with acyl chlorides, esters, aldehydes and ketones. As well as their greater scope of reaction, borohydrides have the advantage of being soluble in many organic solvents in addition to aqueous media. The reagents discussed in this paper are soluble in water, lower alcohols and amines.* Only aqueous and alcohol systems are being considered in this study.

The borohydrides (BH_4^-) decompose in water (H_2O) or alcohol (ROH) to yield various boron products and hydrogen gas (H_2) (see equations (1) and (2)):



The decomposition in aqueous media is more rapid than in alcohol. Furthermore, methanol will react more vigorously with borohydrides than will ethanol. Decomposition may also be accelerated by the presence of acid. The equation for the effect of acid in aqueous media (H_3O^+) is as follows:



*Long chain quaternary ammonium borohydride derivatives⁸ which are soluble in hydrocarbon solvents have been synthesized but are not commercially available.

The breakdown of borohydrides is very important to the paper conservator because the mechanical action of liberated hydrogen bubbles could physically degrade fragile artifacts. However, as equation (3) shows, the pH of an aqueous borohydride will increase (*i.e.* acid is consumed and hence $[H^+]$ falls) as decomposition proceeds, the reaction rate becoming relatively slow as the pH approaches 9.0 (the pKa of boric acid, H_3BO_3). Borohydride solutions should therefore not be used immediately after being made up but be allowed to equilibrate (by self-buffering) until the hydrogen evolution has slowed down. The reduced concentration is unimportant. The conservation may further minimize hydrogen evolution during treatment by using distilled or deionized water when an aqueous system is required. This prevents decomposition of the borohydrides by heavy metal catalysis. As discussed above, the rate of gas formation may also be slowed down by using alcohol solvents, especially ethanol. The addition of acidic papers to the anti-chlor bath would initiate a further vigorous reaction (see equation 3) and so all objects must be deacidified before treatment.* A careful selection process to eliminate objects which cannot withstand even very minor gas evolution would be necessary.

Little information is available concerning the relative thermodynamic and kinetic properties of the three borohydrides (*i.e.* whether or not the reducing action will proceed and if so, how fast). The differences in their reactivity to solvents indicates that their abilities to eliminate chloramine-T from papers may not be identical. However, the available information^{10,11} suggests that the tetramethyl and tetraethyl ammonium derivatives perform similar reductive functions as sodium borohydride (which has been shown to eliminate chloramine-T from paper fibres).

*Since the active bleach in the chloramine-T bath is hypochlorite, it is important to deacidify before bleaching in order to prevent excessive fibre degradation⁹. A single deacidification treatment before the bleaching will be sufficient for both procedures.

II. Experimental

The experiments and data analysis described in this section may be summarized as follows:

1. Preparation of samples
 - a) selection of uniformly yellowed sheets of paper which were cut into strips of four samples.
 - b) determination of initial brightness of each sample.
2. Bleaching
 - a) pre-soaking of samples in water
 - b) bleaching with chloramine-T
 - c) anti-chlor treatment
 - d) washing and drying of paper
 - e) determination of brightness*.
3. Ageing of samples
 - a) interleaving of sample strips with acid-free tissue
 - b) storage in a drawer for five months
 - c) determination of brightness of each sample**.

2.1 Sample Preparation

The experiments described were performed on a mixed fibre*** (wood pulp and linen) paper from a cloth

*The numerical difference between the values obtained in 2(e) and 1(b) is designated as brightness increase upon treatment (see Sec. III, Fig. 1).

**The numerical difference between the values obtained in 3(c) and 2(e) is designated as brightness change upon ageing (see Sec. III, Figs. 2 and 3).

***The fibre analysis was performed by Rosemary Ravindra, Environmental Deterioration Research, CCI, using light microscopy techniques.

bound scrapbook, *circa* 1875 (place of manufacture unknown). Strips of four experimental samples (each sample dimension: $\sim 55 \times 50$ mm) were prepared for each treatment sequence* to be studied. The initial reflectance (or brightness) of each sample was determined at 416 nm using a Beckman Acta MVI Spectrophotometer with an integrated sphere reflectance attachment and using barium sulfate as reference standard. The 416 nm wavelength was chosen to allow comparison of results from this study with data obtained previously⁴.

2.2 Bleaching of Samples

The bleaching and anti-chlor baths were maintained at 22°C for all experiments and distilled water used unless otherwise stated. Paper strips (containing a set of four samples each) were prepared for bleaching by soaking in water for about 5 min.** Each set of samples was bleached for 10.0 min. in 4% aqueous chloramine-T and then quickly immersed in an anti-chlor bath*** containing one of the following reducing agents at 0.1, 0.5, 1.0 or 2.0% (w/v) concentrations:

1. sodium sulfite (Na_2SO_3)
2. sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4 \cdot \text{H}_2\text{O}$)****
3. sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)
4. sodium borohydride (NaBH_4)
5. tetramethylammonium borohydride (Me_4NBH_4)
6. tetraethylammonium borohydride (Et_4NBH_4)

*Any variation in solvent system or in reducing agent type or concentration constitutes a new sequence.

**Pre-soaking of samples ensures that when the papers are placed in the chloramine-T bath, they will be quickly and evenly wetted with bleach.

***One set of samples (*i.e.* a chloramine-T control) were bleached but were not immersed in an anti-chlor. Other treatments proceeded as for the other samples.

****Sodium hydrosulfite is an equivalent name.

A complete series of experiments was carried out at all the reaction conditions described above using water as the anti-chlor solvent. A partial series (borohydride compounds only, at 0.1, 0.5, 1.0 or 2% concentration) using methanol* as solvent was also performed. After 15.0 min. in the anti-chlor bath, the samples were removed, washed in running tap water for at least 90 min, dried between acid-free blotters (several changes of blotters over 18 hours), and then the reflectance was measured.

The samples were interleaved with acid-free tissue and stored in a drawer ($T^{\circ}C \sim 22$ and R.H. from 30 to 60%) for five months. The reflectance at 416 nm was again determined at the end of this period.

III. Results and Discussion

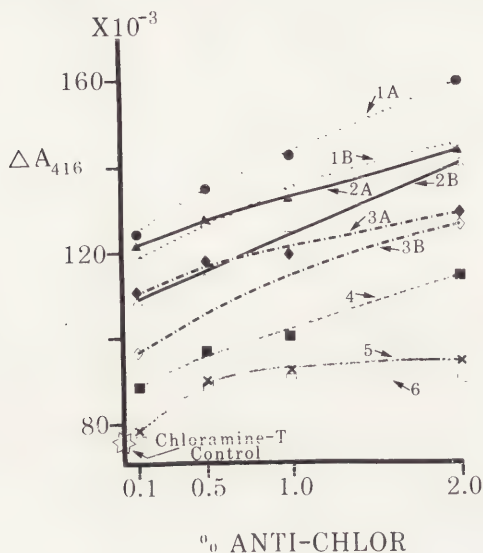
3.1 Brightening of Paper During Treatment.

The combined bleaching effect of chloramine-T and anti-chlor is shown in Figure 1. Here, expressed in absorbance units at 416 nm, is plotted the change in reflectance of the paper samples before and after treatment (ΔA_{416}) plotted as a function of anti-chlor concentration weight-percent. Each data point is the average of the 4 values obtained from each sample set (*i.e.* the paper strip containing 4 samples). At all concentrations of anti-chlor, except for 0.1% sulfite, the change in brightness was greater than for the chloramine-T control (bleached paper, no anti-chlor). The reducing agents are acting as bleaches by reacting with the coloured components** of the yellowed paper via reductive pathways. The chloramine-T performs this same function but by oxidative mechanisms.

*Ethanol can also be used with similar results and is preferred because of its lower toxicity and slower rate of reaction with the borohydrides.

**Many reactions involving the uncoloured constituents of paper fibres also occur during the anti-chlor or chloramine-T bleaching processes.

Figure 1: The Total Increase in Brightness (ΔA_{416}) of Chloramine-T Bleached Papers Treated with Reducing Agent Anti-Chlors.



1. NaBH_4 , 2. Me_4NBH_4 , 3. Et_4NBH_4 ,
 4. $\text{Na}_2\text{S}_2\text{O}_3$, 5. $\text{Na}_2\text{S}_2\text{O}_4$, 6. Na_2SO_3 ;

A = Aqueous media, B = Non-aqueous (methanol) media
 (#4, #5 and #6 were carried out in aqueous media).

A. Bleaching Effects of Borohydride Anti-Chlors.

Figure 1 shows that the borohydride anti-chlors are more effective bleaching agents than are the sulfur-based compounds. This is probably due to the more extensive scope of the borohydride reducing capabilities and in particular, to chemical changes in aldehyde and ketone chromophores which are contributing to the yellow colour of the paper. As previously discussed, the sulfur anti-chlors are not able to perform these reductions.

The relative order of the three borohydrides in terms of increasing change in brightness during treatment is $\text{Et}_4\text{NBH}_4 < \text{Me}_4\text{NBH}_4 < \text{NaBH}_4$.

The aqueous treatments result in greater over-all brightening than do the non-aqueous, alcoholic processes. All of these observations correlate well to the observed rates of relative reactivity of borohydrides to solvents (see introduction) and to the differences in effective borohydride anion concentration among the three anti-chlors. For example, at 2% w/v the actual concentration of NaBH_4 is 0.53M (M.Wt. = 38g/mole), while for Me_4NBH_4 and Et_4NBH_4 , it is 0.22M (M.Wt. = 89g/mole) and 0.14M (M.Wt. = 145g/mole) respectively. Since the variation in molar concentration is so large it is very difficult to determine if there is any significant difference among the reagents (*i.e.* in terms of their reactivity to coloured components of the paper).

B. Bleaching Effect of Sulfur Anti-Chlors.

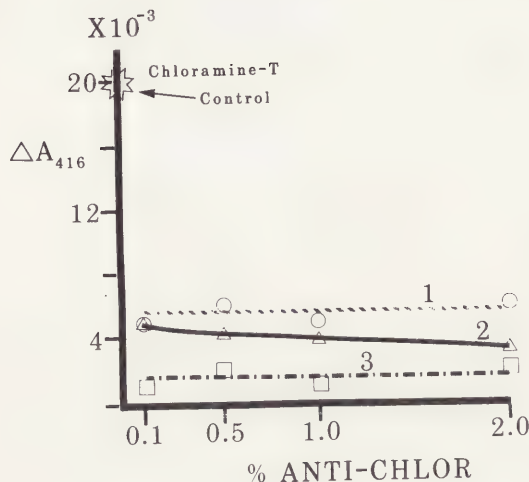
The chloramine-T/sulfur anti-chlor treatments demonstrate increasing overall brightening in going from Na_2SO_3 to $\text{Na}_2\text{S}_2\text{O}_4$ and then $\text{Na}_2\text{S}_2\text{O}_3$. This order may be predicted on the basis of relative redox potentials of the three systems ($\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_2\text{O}_4^{2-} \rightarrow \text{SO}_3^{2-}$, see introduction). As discussed previously, the concentrations are in weight percent and since the molecular weights are quite different (248, 192 and 126g/mole for $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, $\text{Na}_2\text{S}_2\text{O}_4 \cdot \text{H}_2\text{O}$ and Na_2SO_3 respectively), the molar concentrations will vary considerably at a specific weight percent.* (For example: at 2% the respective molarities of $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_4^{2-}$ and SO_3^{2-} are 0.08, 0.1 and 0.16 moles/liter). Despite these large differences, the $\text{S}_2\text{O}_3^{2-}$ (at the lowest molar concentration) still results in the greatest change in brightness. The standard redox potential, and perhaps some kinetic factors not explored in this study, appear to be the decisive factors in the removal of discolouration by the sulfur anti-chlors.

3.2 Change in Brightness of Paper During Ageing.

The results for the change in brightness of paper samples during 5 months' storage are shown below in Figures 2 and 3. The paper treated with the sulfur

*A study based on relative bleaching effect of reducing agent on a molar basis (rather than weight-percent) is presently in progress in the Conservation Processes Research Section of CCI.

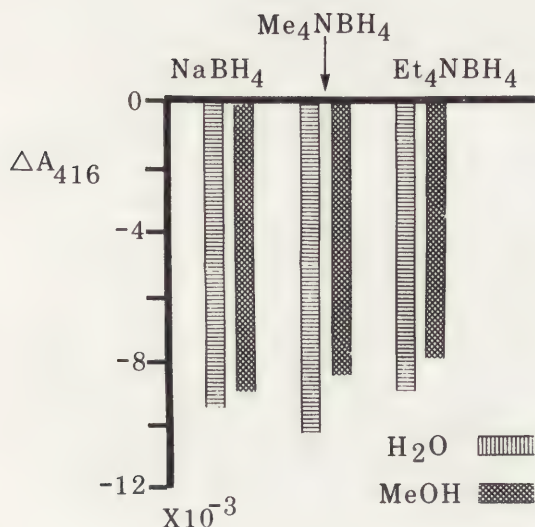
Figure 2: The Increase in Brightness (A_{416}), After Five Months' Storage, of Chloramine-T Bleached Papers Treated with Sulfur-Based Anti-Chlors.



1. Na_2SO_3 , 2. $\text{Na}_2\text{S}_2\text{O}_4$, 3. $\text{Na}_2\text{S}_2\text{O}_3$

reagents (Fig. 2) became brighter during the ageing period. The samples anti-chlored with sulfite brightened the most, followed by dithionite, and then thiosulfate. (All values are below that for the chloramine-T control experiment). Previous work ^{2,4} has suggested that brightening of chloramine-T bleached samples during storage is due to incomplete removal of bleach residues. This is supported by observations that the extent of bleaching during ageing correlates with the strength of the reducing agent (*i.e.* the strongest reagent leads to the least brightening during storage). This order of extent of bleaching also agrees very well with the magnitude of the bleaching effect of the anti-chlor treatment itself (*i.e.* $\text{S}_2\text{O}_3^{2-} > \text{S}_2\text{O}_4^{2-} > \text{SO}_3^{2-}$: See Sec. 3.1), another indication that the redox potential of the anti-chlor is an important determining factor in the extent of removal of residual chloramine-T.

Figure 3: The Decrease in Brightness (ΔA_{416}), After Five Months' Storage, of Chloramine-T Bleached Papers Treated with Sulfur-Based Anti-Chlors.



Furthermore, the small variation in brightening as a function of anti-chlor concentration indicates that the scope of reaction of a specific reagent is more important than how much of the anti-chlor is present.

Borohydride treatments gave results in direct contrast to the data for the sulfur anti-chlors, since the samples yellowed slightly during storage. For each of the three borohydrides used, anti-chlor concentration had no effect on the resultant ΔA_{416} value; thus, for each treatment ΔA_{416} values have been averaged for all concentrations and are shown in Figure 3.

The small differences in yellowing between the borohydrides and between water and alcohol solvents are the same order of magnitude as the experimental

error and therefore of no real significance. Differences in the rates of borohydride decomposition and in the rates of bleaching of paper by the anti-chlor had therefore no measurable effect. All borohydride systems tested are equally effective at removing chloramine-T residues.

The amount of yellowing observed after ageing is not excessive, when compared to that observed after other chlorine bleaching treatments⁴. However, it is significantly higher than that which would be observed after treatment with the reducing agent alone* (average ΔA_{416} of 8 to 16×10^{-3} compared to $\sim 2 \times 10^{-3}$ for borohydride alone). Although this difference is not large, it does show that the oxidative bleaching (*i.e.* chloramine-T) is degrading fibres and does result in accelerated yellowing. The reducing capabilities of the borohydrides would reverse some of this degradation** but would not be capable of completely restoring the fibre chemically or physically.

The observations that the anti-chlor invariably adds to the overall bleaching of paper fibres plus the knowledge that the yellowing of the chloramine-T/borohydride treated samples exceeds that of the anti-chlor alone suggests that chloramine-T bleaching be abandoned in favour of reducing agent bleaching (specifically borohydrides). However, the combined chloramine-T/borohydride treatment does result in better brightening

*Work has been completed by the author on the bleaching efficiency of the three borohydride systems (in both aqueous and alcoholic media) and has been presented at the Annual Meeting of IIC-Canadian Group, May 1980 in Victoria, British Columbia. Publication of the data will be forthcoming.

**The chemical effects of oxidation of cellulose (the most important component of paper fibres) may be categorized as formation of aldehyde, ketone and carboxylic acid groups as well as breakage of the polymer chains. Borohydrides are able to reduce the aldehyde and ketone groups back to the alcohol but cannot react with carboxylic acids or polymerize cellulose.

of fibres than anti-chlors alone. The extent of bleaching with borohydrides could be improved by increasing the reagent concentration but this would not be advisable since high concentrations of borohydride would elicit excessive hydrogen gas evolution which could damage fragile artifacts. It must also be recognized that a five-month ageing period is not sufficient to allow firm conclusions as to rate of yellowing. It is not clear that the papers treated with the chloramine-T/borohydride combination will continue to revert (*i.e.* yellow) at a rate exceeding that of the anti-chlor alone*.

Stain-removal by reduction has, in the past, been characterized as having poor colour stability¹². Promising as the results are, it remained to be proven by additional testing that treatment with borohydride does not eventually lead to serious reversion.

Another point is that the conservator will occasionally come across stains which will respond better to an oxidizing bleach than to one that works by reduction. Therefore, the use of chloramine-T may still be justified in certain situations (providing an adequate anti-chlor is used after treatment) where slightly better brightening is required and the stains do not respond sufficiently to the reducing agent alone.

Summary

The following conclusions may be drawn from the previous discussion:

1. The use of reducing agent anti-chlors following oxidative bleaching adds to the total bleaching effect. The relative order of the anti-chlor systems, in terms of their increasing ability to decolourize stains (as a function of weight percent concentration) is:



The borohydride treatments which were carried out in aqueous media bleached more than those in non-aqueous (alcohol).

*In order to determine if this trend continues, the brightness change for all of these samples will be measured at 12 months of storage.

2. During 5 months of dark storage, papers treated with sulfur anti-chlors had continued to bleach, suggesting that the sulfur anti-chlors are not able to fully remove chloramine-T residues from the paper.

3. During 5 months of dark storage, papers treated with borohydride anti-chlors did not continue to bleach (but yellowed slightly), suggesting that full removal of chloramine-T residue had taken place.

The overall conclusion is that chloramine-T may be used as an effective bleach if an adequate anti-chlor process (*i.e.* a borohydride at a concentration of at least 0.1%) is part of the treatment. However, the impressive bleaching power and brightness stability of the borohydride indicate that a better approach would be to use the reducing agent alone. The problem of possible physical damage to fragile artifacts by hydrogen gas liberation can be met by careful selection of treatment conditions. Further testing is required before borohydrides may be used on extremely degraded materials.

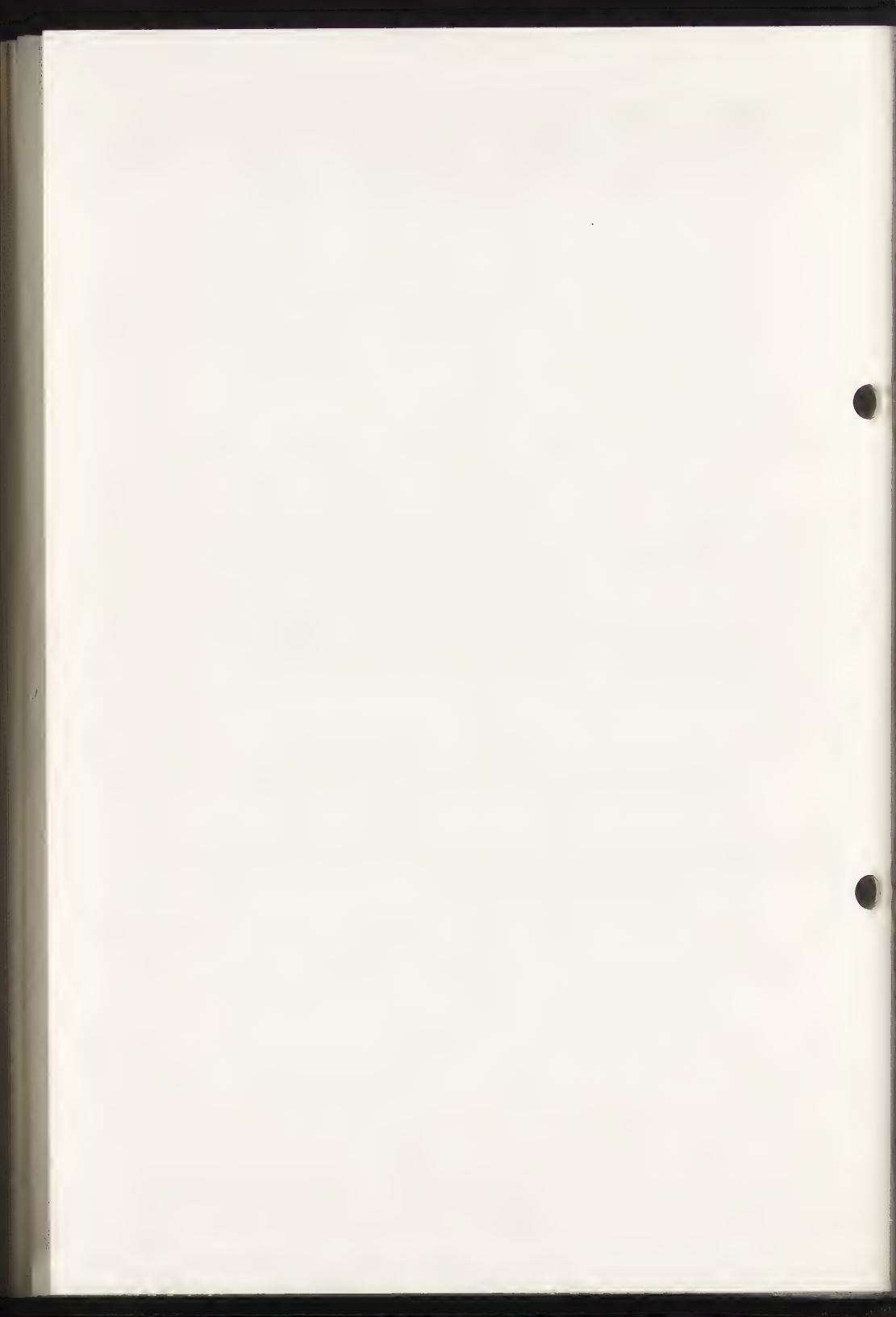
Acknowledgements

The author would like to acknowledge the assistance of J. Clifford McCawley, Chief, Conservation Processes Research, C.C.I., in the writing of this paper. She would also like to thank David W. Grattan for helpful comments and discussion during the carrying out of this work.

References

1. Hofenk-de Graaff, Judith H., "The Effect of Chloramine-T on Paper," ICOM Committee for Conservation, 4th Triennial Meeting, Venice, vol.15, no.4, 1975, pp.1-17.
2. "An Informal Discussion on the Bleaching of Paper," Second Seminar on the Scientific Approach to the Preservation of Paper Artifacts, Institute of Paper Chemistry, Appleton, Wisconsin, IIC-American Group, Nov.8, 1972.
3. Daniels, Vincent, "The Elimination of Bleaching Agents from Paper," The Paper Conservator, vol.I, 1976, pp.9-11.

4. Burgess, Helen D., "The Colour Reversion of Paper After Bleaching," The Conservation of Library and Archive Materials and the Graphic Arts, Proceeding of the Cambridge 1980 Conference, 1981, in press.
5. Nickless, G., Ed., "Inorganic Sulphur Chemistry," Elsevier Pub. Co., New York, 1968.
6. Gaylord, Norman G., "Reduction with Complex Metal Hydrides", Interscience Pub. Inc., New York, 1956.
7. Hajós, Andor, "Complex Hydrides", Studies in Organic Chemistry Series (vol.I), Elsevier Scientific Pub. Co., New York, 1979.
8. Sullivan, E.A., and A.A. Hinckley, "Reduction with Quaternary Ammonium Borohydrides," *J. Org. Chem.*, vol.27, 1962, pp.3731-33.
9. Hey, M., "Paper Bleaching: Its Simple Chemistry and Working Procedures," *The Paper Conservator*, vol.II, 1977, pp.10-23.
10. Technical Literature: "Tetraethylammonium Borohydride and Tetramethylammonium Borohydride," Bulletin no.7-A, Ventron Metal Hydrides Division, Thiokol, Alfa Products, 152 Andover Street, Danvers, M.A. 01923, U.S.A.
11. Banus, M.D., R.W. Bragdon, and T.R.P. Gibb, "Preparation of Quaternary Ammonium Borohydrides from Sodium and Lithium Borohydrides," *J. Amer. Chem. Soc.*, vol.74, 1952, pp.2346-48.
12. Trotman, E.R., "Reducing Bleaching Agents", Textile Scouring and Bleaching, Griffin & Co. Ltd., London, 1968, pp.118-25.



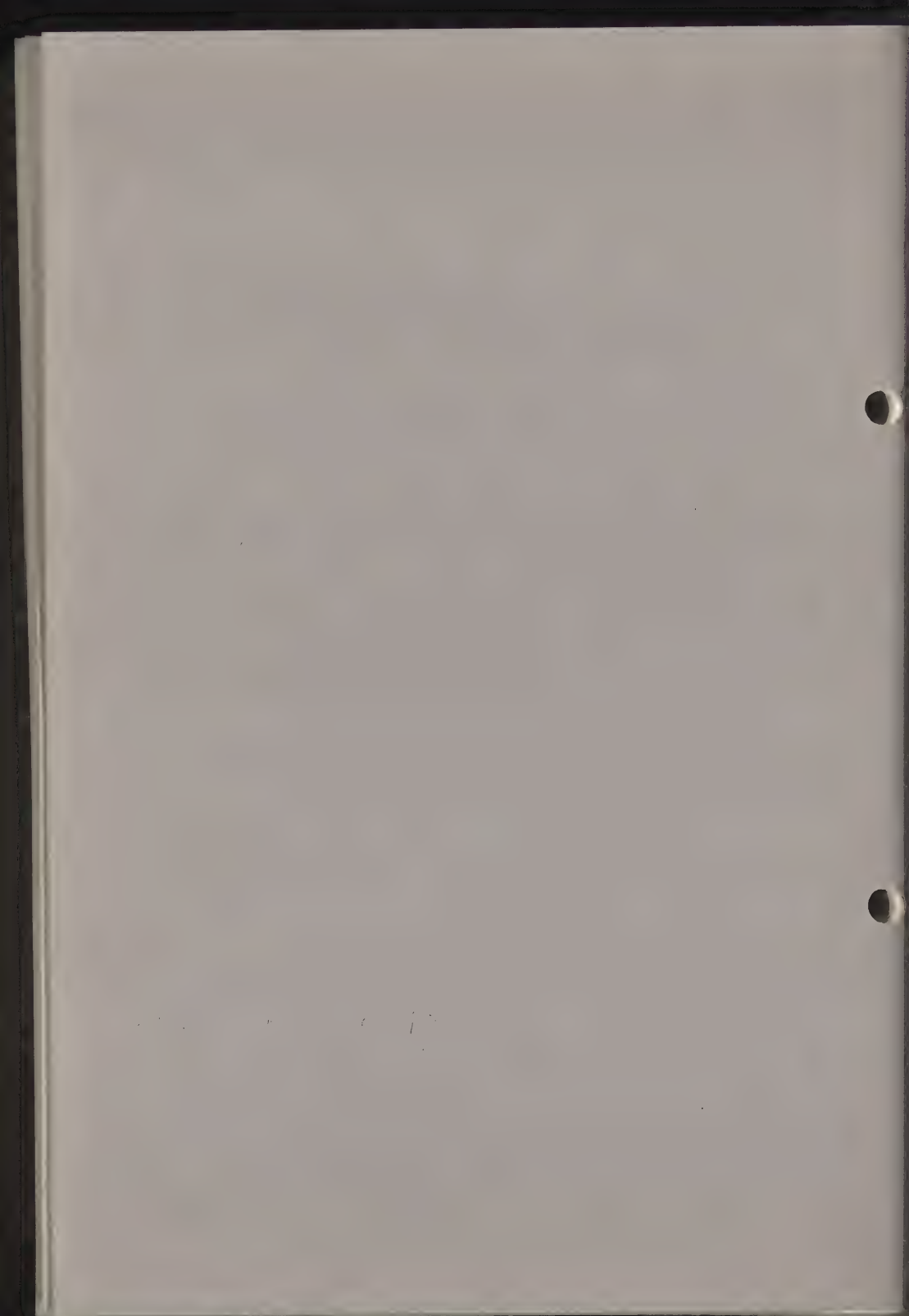
81/14/13

REMOVAL OF TRANSPARENCY OF MANUSCRIPTS
AND DOCUMENTS ON PARCHMENT

M.V.Yusupova

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



REMOVAL OF TRANSPARENCY OF MANUSCRIPTS AND DOCUMENTS ON
PARCHMENT

M.V.Yusupova

State Historical Museum
1/2 Red Square
Moscow
USSR

Analysis of possible ways of transparency removal was carried out. It is shown that in case of one-sided documents of charter type it is possible to decrease transparency by way of back surface loosening and applying to it finely dispersed filler. A new universal method of transparency removal is described incorporating parchment extension. The opportunity to use this method for any kinds of documents including two-sided manuscripts is pointed out.

One of the most widespread damages of parchment is considerable and non-uniform increase of transparency which spoils its outview and makes difficult the reading of two-sided documents. It results usually from unfavourable preservation conditions and rather often from the

process of various restoration operations such as softening, compaction, utilization of certain reagents and interleaving materials.

Obviously, the simplest and most efficient way to prevent transparency emergence is to create optimum restoration and preservation conditions. Removal of transparency already existing causes considerable difficulties.

In restoration practice two methods of transparency removal are known. In first case it is recommended to treat damaged areas of parchment alternately with the composition of casein, borax, ammonium bicarbonate, cedar oil, hexane, water, alcohol and nipagin and alcohol solution of borax, boric acid and nipagin. However, as there are no grounds for these reagents complex utilization, its being rather time-consuming and demanding special restorer's flair casts doubt on the efficiency of this method.

The other method consists in application to transparent areas of parchment of airy-dry finely dispersed filler - calcium carbonate powder (chalk). Naturally, the text's legibility decreases after such treatment and chalk powder crumbles gradually. Nevertheless for one-sided documents of charter type we shouldn't exclude the possibility to remove transparency in this way. Indeed, when applying the filler to the back side of the transparent surface taking into account parchment porosity and filler dispersion and when using a suitable binding agent to fix the filler on the surface we may receive the desired effect. In connection to this we have carried out special investigation.

As fillers calcium carbonate and silicon dioxide powders were used, their specific surface being from 30 up to $380 \text{ m}^2/\text{g}$ for parchment porosity of 25-75 per cent. The investigation showed that satisfactory fixation of the filler is provided by synthetic polymeric phtorlon

materials. However, despite the wide range of the filler dispersion and phtorlon utilization our attempts to remove transparency gave no result as it had already happened earlier due to difficulties in uniform distribution of finely dispersed powder on parchment transparent surface. Since removal of transparency by way of applying and fixing the filler appears rather difficult and allows limited utilization we find it unreasonable to continue the investigation in this direction.

The opportunity to approach the problem of transparency removal quite differently opens up when analyzing the factors accompanying its emergence. We found that in case of transparency increase some important structural-mechanic changes in parchment take place, in particular, porosity decreases considerably. In this connection to decrease transparency it is possible to try restoration of damaged structure, at least partially. This is what we attempted to do.

The objects of our investigation were a velvety thora of the end of 19 century, a new parchment of home production and parchment bindings of 17-19 centuries. Model manuscripts with two-sided texts were prepared on new parchment. To provide for satisfactory water resistance the texts were written in ball-pen paste. Parchment was made transparent by way of keeping it for 30 minutes under water with subsequent drying-up under high pressure in a press. When evaluating parchment properties, transparency (transparency factor for effective wave length of $633 \text{ m}\mu$), tensile strength, elasticity (relative lengthening under tension), hygroscopicity, water yielding capacity and porosity were measured. Transparency factor was defined photometrically while other values were defined by the methods accepted for leather.

One of the analyzed methods of transparency removal was based upon the assumption that transparency should decrease in case of loosening the parchment's back sur-

face with an abrasive to increase its porosity. Since such treatment may be applied to one-sided documents we tested only the thora and binding parchments. As abrasive pumice-stone and emery (aluminium oxide) were used being quite inert to parchment.

The investigation showed that in case of minor porosity increases mechanical treatment allows to decrease transparency considerably (1.5-2 times). Such treatment results in surface thickness and texture changes but physical and mechanical properties stay practically constant (see table 1).

Table 1. Effect of abrasive agents treatment on parchment properties in case of transparency removal

Parch- ment	Group of samples	Thick- ness '(mm)	Strength (kgs/mm ²)	Relat- ive length- ening '(per cent)	'Hygro- scopic- ity (per cent)	'Water yield- ing cap- acity '(per cent)
Writing parch- ment (thora)	Before treat- ment	.40	3.6	15.2	8.4	3.8
	After treat- ment	.32	3.8	15.8	8.9	3.3
Binding parch- ment	Before treat- ment	.37	3.0	19.4	10.6	4.4
	After treat- ment	.22	3.4	17.6	12.5	6.0

Transparency decrease gains in strength after application to the loosened surface of finely dispersed filler (e.g. chalk with specific surface of 30 m²/g) and subsequent careful knocking the parchment out (with a glass or wooden stick) to prevent the crumbling of the filler. So, the treatment with inert abrasive agents allows to decrease transparency of one-sided parchment.

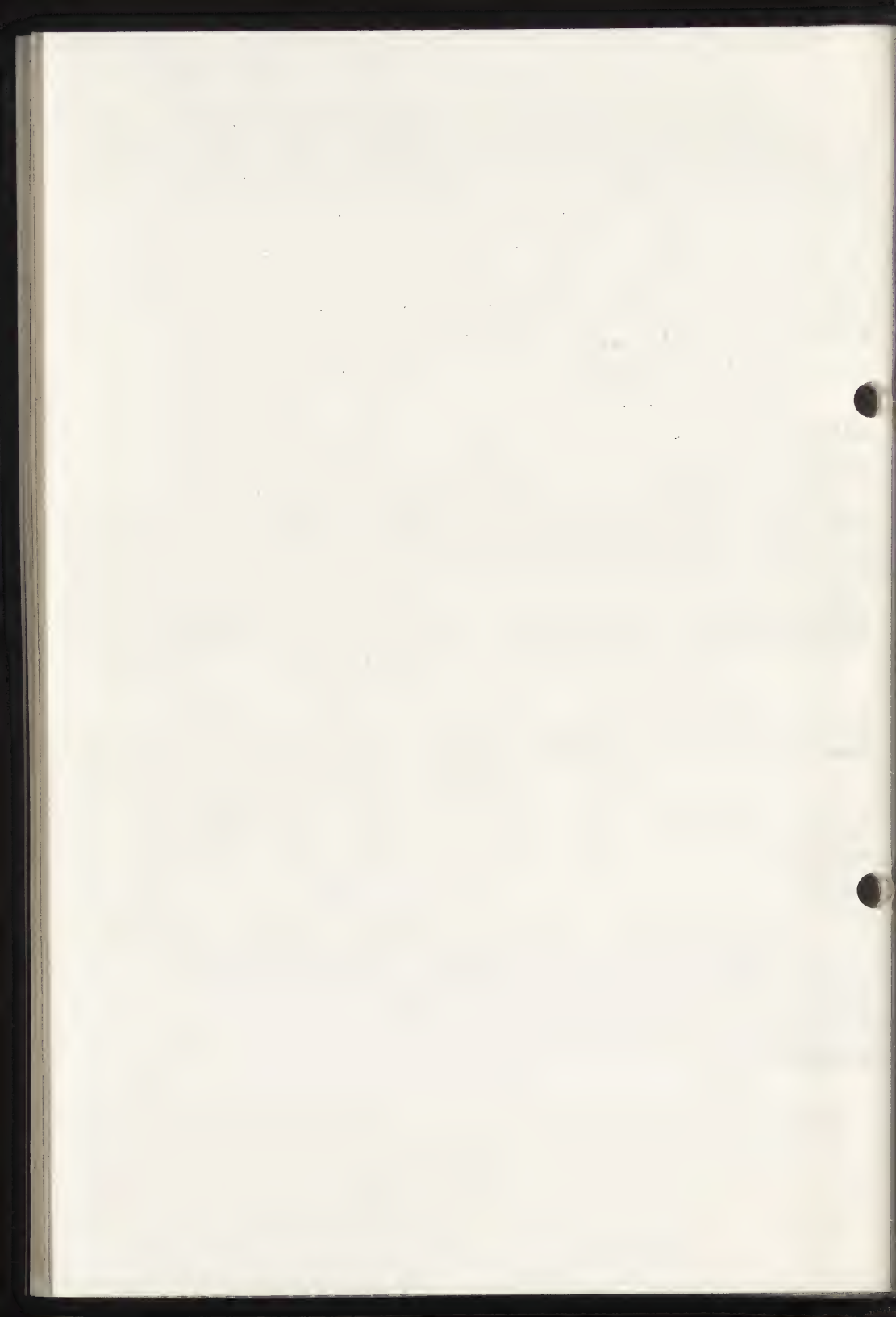
Another way we discovered to remove transparency of any kinds of documents consists in extending parchment. We noticed their uniform turbidity which obviously resulted from micro-inhomogeneity areas emergence, that is microareas whose reflective index differs from that of the rest of the material. The same phenomenon is known for some other polymers such as cellulose acetate, polymethyl metacrylate (acrylic plastic), polystyrene when they are, like parchment, in a sufficiently elastic state.

When creating certain optimum extension conditions slightly differing for each material it is possible to decrease transparency considerably (more than two times), to restore two-sided manuscripts legibility and at the same time to preserve thickness, texture, strength, elasticity and obviously durability of parchment (see table 2).

Table 2. Effect of extension on writing parchment properties in case of transparency removal

Group of samples	'Thickness' (mm)	'Strength' (kgs/mm ²)	'Relative lengthening' (per cent)	'Hygroscopicity' (per cent)	'Water yield. capacity' (per cent)
Before extension	.21	7.7	26.2	13.5	8.2
After extension	.21	8.1	25.0	15.6	9.4

Extension method of transparency removal is sufficiently simple, efficient, universal and will evidently be applied in restoration practice of manuscripts and parchments.



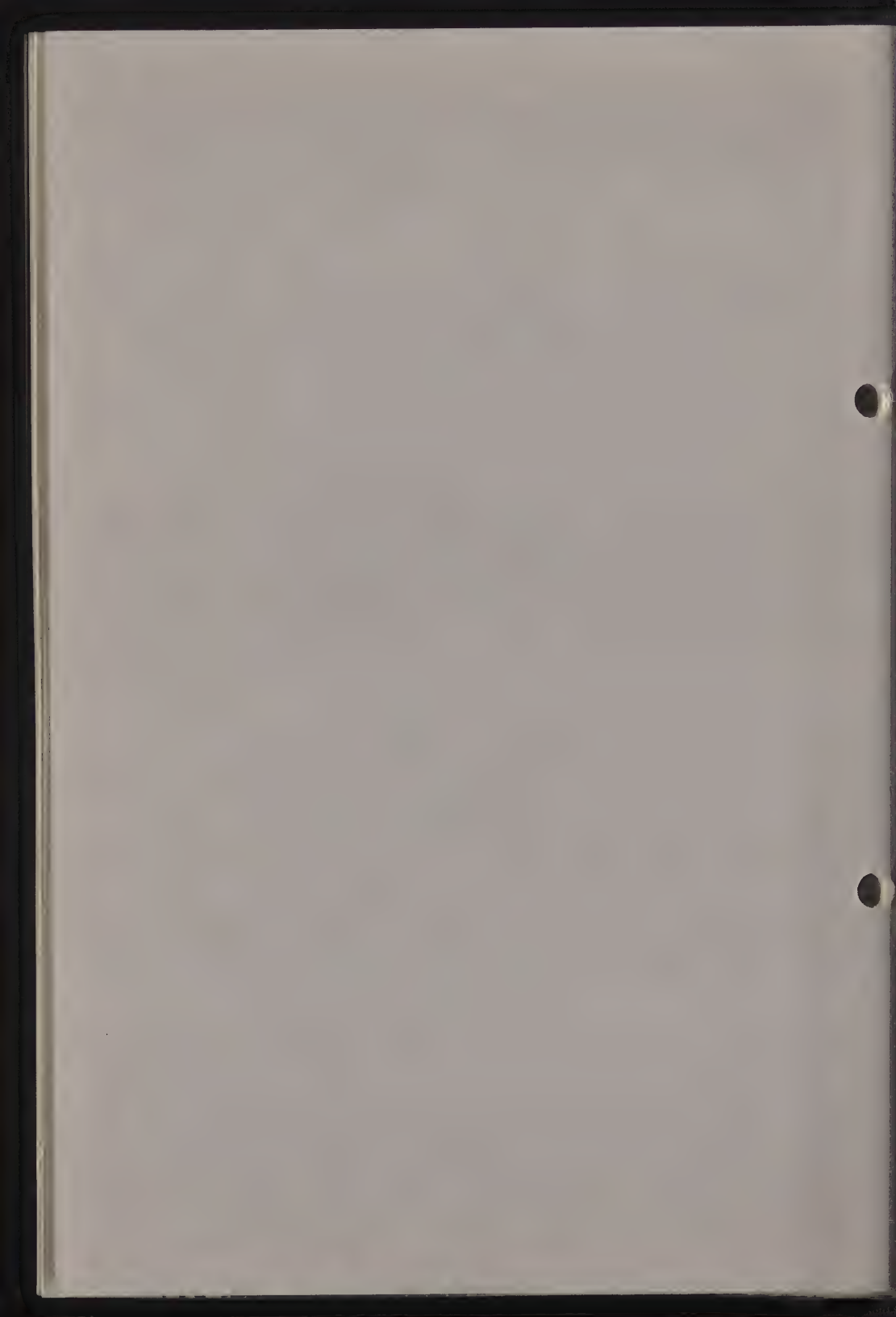
81/14/14

RESTORATION OF THE WORLD CHRONICLE OF SCHEDEL

Imola Simon

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



RESTORATION OF THE WORLD CHRONICLE OF SCHEDEL

Imola SimonSimmelweis Orvostörténeti Múzeum
Hungary

The translation of the World Chronicle of Schedel by Georg Alt was printed in the workshop of Anton Koberger, a Nürnberg printer, in 1493. The blind-stamped, wood-boarded binding of the volume of 45 x 32 cm dimensions is a so-called "historical binding", made in the years around 1530. The body of the book was in one piece, its front wooden board was split in two pieces and its leather cover was in a bad condition. The volume was insect-infected, some of the pages were completed at the occasion of binding. The paper contained water-spots and its structure was damaged.

While taking to pieces, the mounting parchment straps were stripped; the latter originated from cutting up a handwritten copy of "De physico auditu" (lib. VII.) by Aristotle, from the XIII. century. Material of the book: water-marked ragpaper; wooden parts made of beech-wood, 1520 to 1540; cover: pigskin; metal clasps made of copper. After dry and wet cleaning, the paper material was reinforced by Glutofix, with protection of the water-coloured figures. The missing parts of the wooden board were completed and the volume was rebound. After restoration, the condition of the volume enables exhibition.

The book with title-page missing beginning with the words: "SCHEDEL Hartmann: Register des buchs der Chroniken und geschichten mit figure vnd pildnussen von anbegin der welt bis auf dise unsere zeit...", mentioned under the name of World Chronicle of Schedel by the special lite-

rature, is guarded in the book stock of the Semmelweis National Library of Medical History, in its cabinet of ancient and rare books. (Inventory number 1752.)

As it appears from the entry the book begins with a name and subject index and the title of the book may be read in its headline. According to the colophon on the verso of the 2nd page of the map to be found at the end of the book, this latter was printed in the workshop of Anton Koberger, a Nürnberg printer, in 1493.

I found watermarks of five kinds in the book itself and a sixth watermark in the endpaper.

Besides the typographical comparison it was just by the help of the watermarks that it was possible to prove the fact that the two run-in pages in the volume on the pages CXC and CXVII, where the fallen out pages were replaced by smaller ones inserted in their places as complements, originated from another issue of the same edition.

Description of the binding

The Nürnberg print of 1493 of the Schedel's World Chronicle has the dimensions of 45 x 32 cm measured on the book cover and a bulk of 8 cm.

It is full-leather-bound, stitched on five double ribs and it was clasped by two snaps. The unpainted full-leather board was decorated with blind-stamping both in front and at the back. The book spine was not decorated and two parallels were only stamped along the ribs. It had originally a sewn cap. The bookbinding was, as usual in that age, a binding of fixed spine, sewn on real ribs. There were two brass clasps at the front on the remained part of which is visible that it was very finely decorated by chiselling and engraving. There are and there were no mountings on the binding. The bookbinder used a smooth white hand-made paper for the inner endpapers. The binding technology is on the whole of German Gothic character; the decoration and its layout on the front board bears already the marks of the Renaissance, on the other hand the rear board shows a Gothic arrangement yet.

Blind-stamped decoration

Our copy has a decoration made prevailingly with a roller which had a relatively simple pattern. The impression is not too deep which is among others the consequence of using a relatively broad roller 2 centimetres wide. It was essentially the blind-stamping being effective only on the surface that caused the almost total abrasion of the decoration from the front board by this time.

State of the book

The body of the book is in one piece, but the front board split lengthway in two with the consequence that the leather covering the board ripped both at the head and the foot. The leather cover of the book is in a very bad condition; the cover of the front board is almost totally worn down; there is a break of considerable size in the leather at the foot; the stamping is totally missing from the foot of the book; there are gaps showing in all four corners. The spine of the book shows also very great ravages of time; the stampings are missing both at the head and the foot; the cap broke down and lost; the leather is worn down respectively broken above the ribs and near the boards.

It is only a part remained of the pair of snaps clamping the book in front that is the lower snap fastened to the front board. The others came off and lost.

The book was attacked by insects. The leather cover and the wooden board were bored through and through, what is more, there were also serious damages caused by these pests in the paper material of the book. The corners of the wooden board broke and came off, they were worn down and the front of the rear board became also defective. The loose sheets of the endpapers are missing both in front and at the rear.

The book, as a whole, was very defiled, the lower corners of the pages were covered with a very great human soil caused by the frequent handling and thumbing; the outer leather cover was similarly strongly darkened by the dirt. The book was supposedly hit by moisture around the middle of the length of the book-body in a length of about 15-20 cm.

Consequently the paper became water-stained and its structure weakened considerably. The edges of the are ragged especially in the last third of the book, with tears of 1-2 cm by places and with lesser breaks of continuity.

Disjointing of the book, taking off the parchment

After I had removed the leather cover from the saddle, it appeared that the spine of the book was backed with a strip of parchment and the book-body was fastened by this to the wooden board.

Both the parchment and the board were covered with a thick layer of starch under the endpaper. After having gradually moistened the swelled layer of starch with alcoholic water I removed it with a scalpel. By this method it was possible to take off safely the paper on both boards from the side beside the endpaper; not even the writing got damaged; it became clear and readable and the cleaning did not meet with difficulties.

Taking the parchment off the wooden board was more complicated and difficult and involved inevitably a certain loss suffered by the text on the parchment sheet; while in the previous case the weaker material (paper) wanting no forbearance was on the top, now the material needing consideration was on high. The mild moistening offered itself for the most suitable process.

After I had taken the parchment off the wooden board, the dismantling of the book cover from the book-body became possible. Then the ends of the binding strings passed through the board were set free. After the removal of the book cover was discovered what a great amount of soil accumulated between the parchment strip and the book-body which damaged seriously also the writing on the parchment.

The removal of the parchment from the book spine raised increased problems. As a result of the attempts the manuscript on the parchment stuck partly to the edges of the sheets. The separation of the two parchments stuck together caused extremely much trouble. Then I tried to take off the parchment while disjointing the book. During the taking off and disjointing the text written on the inner side of the parchment stuck to the

spine of the book became visible; first the red and blue marks indicating - as it became known later - the numbering of the pages of the book, then the coherent text, too. The removed parchment was still dirty, rigid and very uneven.

The further cleaning was made with a scalpel and with alcoholic water. The adhesive had to be removed from the parchment in this way. Meanwhile the principal task to be considered was to preserve safely the writing as it could only become readable for the researcher of the codex in such a way.

I wiped the removed parchment laid on a glass-plate with a 50% solution of alcoholic water, then I covered it with wax-paper and put under weight. The following day the parchment, which was still rather wet, was taken off the glass-plate and put again between clean blotting-papers under weight. This process was repeated up till the time as the moisture content of the parchment reached the relative humidity of the air in the room.

After the assembling of the removed and flattened pieces of parchment it appeared that they were cut out of an old codex leaf by the binder and the text on the strips used for backing the spine could be read together coherently. I sized the parchments together with a silicone adhesive using a narrow strip of Japanese vellum for strenghtening them. The places of the ribs of the book were cut out by the binder. I completed the parchment on these places with Japanese vellum.

Cleaning

The first phase of the cleaning of the paper was the dry cleaning. This was carried out by erasing by hand and with a rubber-machine and the dirt was removed in some places with glass-paper, respectively with a scalpel from the dents of the paper. This latter needed a more cautious treatment in places where it became already weaker from the use. Here the weakened part is strenghtened with Japanese vellum. Parallely with this a resizing was carried out with Glutofix.

The dry cleaning was followed by a wet one. As there are hand-coloured illustrations in several places in the book, the wet cleaning could

be started only after shielding the paint layer. The hand-colouring was made with water-colours (tempera). The colours fixed in general well and a certain peeling off could be observed only in some places. A perceptible discolouration occurred only by the white lead colours; they became oxidized, consequently blackened which could be regenerated by treating them with peroxide of hydrogen.

Finally I shielded the colours with an alcoholic solution of Regnal. Unfortunately, during the treatment with Regnal, the coming through of the colours penetrated still more in the paper, so the colours became stronger also at the back of the illustration (bleeding through).

In this case it proved to be more advantageous not to shield the colours, that is not to seal them from the side of the colours, but to do it later during the fixing of the paint which was eventually still peeling off after drying.

The watery bathing of the unpainted pages started with a longer soaking and the removal of the stubborn stains was carried out locally on a glass-plate with water containing a detergent of Evamin CC. This was followed again by a thorough soaking. In the case of the hand-coloured pages the sequence had to be reversed. First the unpainted parts were cleaned by brushing them with a detergent, then they were rinsed on the same way (by using a brush) with pure water and it was only after this that followed the quick and short-time soaking of the whole page which was necessary for ensuring the uniformity of its colour, for removing the water-stains and for stretching out evenly the paper. The cleaning of the paper on a glass-plate with a quick and short-time water-bath, if carried out with due skill, is not only unharmed but also brightens up the colours. Just before the wet cleaning I could still soften the different stubborn stains with organic solvents and by ironing them through blotting paper. Some strong tawny spots, which could not be softened with any agent till then, were whitened locally. The paper was not spotted at all. The local whitening became mainly effective during the wet cleaning process, because then the cleaning with detergent and the following soaking brought together the whitened and unwhitened parts in their colours. The wet cleaning was finished by drying and pressing the pages between blotting-papers.

Repairing

a/ Repairing of the paper. The strenghtening of the weak parts of the paper was carried out with Glutofix. Glutofix was applied for the repairs and complements, too. I used Japanese vellum of adequate thickness for the repairs and complements. The traces of the insect chews were completed with paper pulp. In the course of the work two methods were developed for this: I. Paper pulp was made with a household mixing-machine; this pulp mixed with methylcellulose was used for filling in the gaps; thereafter a slow drying and the pressing followed. II. A simpler method proved to be more effective for the completion of the lesser gaps. The edge of the break of continuity was smeared with Glutofix, then a fibre mass was made of Japanese vellum applied anyway for the completion. This mass fluffed with a scalpel was stuffed in an adequate quantity into the gap and arranged similarly with the scalpel. The repair dried up already during the work insofar that the paper could be pressed.

After having carried out the repairing and completion I moistened the paper with water spray and dried it in a press.

b/ Completion and repairing of the wooden board. The front board split in two in the middle was clamped together with cardboard strips pasted in layers into a dovetail-like engraving. The defects observed on the edges of the wooden board (breaking off, abrasion) were completed with Duracrol synthetic filling material; thereafter they were polished in order to match to the board.

Binding of the cleaned and repaired book

In the original state of the book the flying sheets of the endpapers were lost, their parts mounted on the board, however, remained. They were made of mould-made white paper corresponding with the thickness and quality of the paper which served as material for the book. Considering this it seemed not to be necessary to take off, clean and complete it, that is not to use it again as endpaper after the restoration. I used new Japanese handmade paper of adequate thickness as endpaper. Corresponding with the original technique I made turned down endpapers.

Again in conformity with the original sewing way I stitched the book with linen thread to the double ribbed hemp-strings twisted to an adequate thickness. The bind distances were marked out corresponding with the original state.

The stitched book-body was sized with Planatol mixed with methylcellulose. After sizing and drying it was rounded and mildly beaten to rim (determined by the wooden boards).

The original book was glued with bone-glue, but this can be attacked by microorganisms during the time. In order to prevent this I used the adhesive Planatol BB-Superior of synthetic base mixed with methylcellulose. This is less rigid and more flexible, so the roundness of the book could more easily right itself and its form could less be maintained as that of a book strengthened with glue. It is just for this reason that I backed the book kept still in press with strong Japanese vellum of adequate thickness, so this mounting layer did not figure in the original binding.

After having dried the book I took it from the press and mounted the wooden board in conformity with the original technique to the binding-strings and these latters were carefully wedged in the holes on the board.

For mounting the back the above-mentioned codex fragment parchment was applied. Considering that its cultural historical value can be only ensured as a separate annexe removed from the spine of the book, it was not remounted but instead of this a Japanese vellum of adequate strength was cut on the base of the cut of the codex fragment and this was led according to the original technique from the inner sides of the front and back boards across the spine.

From the original state of the headband appears that it was sewn with the parchment on the already backed book; that it broke off completely in the course of time and its embroidery and stitching technique became unrecognizable (this latter remained only on the wooden board covered with leather and it was only on the base of these few stitches that their restoration was rendered possible). The new headband based on these traces was made of natural flaxen and hand-coloured blue whipcords.

First I cleaned the leather dry, the dust-control was followed by erasing. In the next phase, having still made efforts for avoiding the wet

treatment, I continued the cleaning with chlorated hydrocarbons, so the removal of the soil from the surface turned out in a satisfactory way, while dissolving the dirt from the clefts of the leather and from the dents of the blind-stamping decoration did not succeed even with this technique as required.

I could not avoid using the wet cleaning the disadvantages of which are well known. For this I used a faintly alkaline baby soap. In order to come close maximally in colour to the original whiteness of the leather used a surface treatment with common salt and alum.

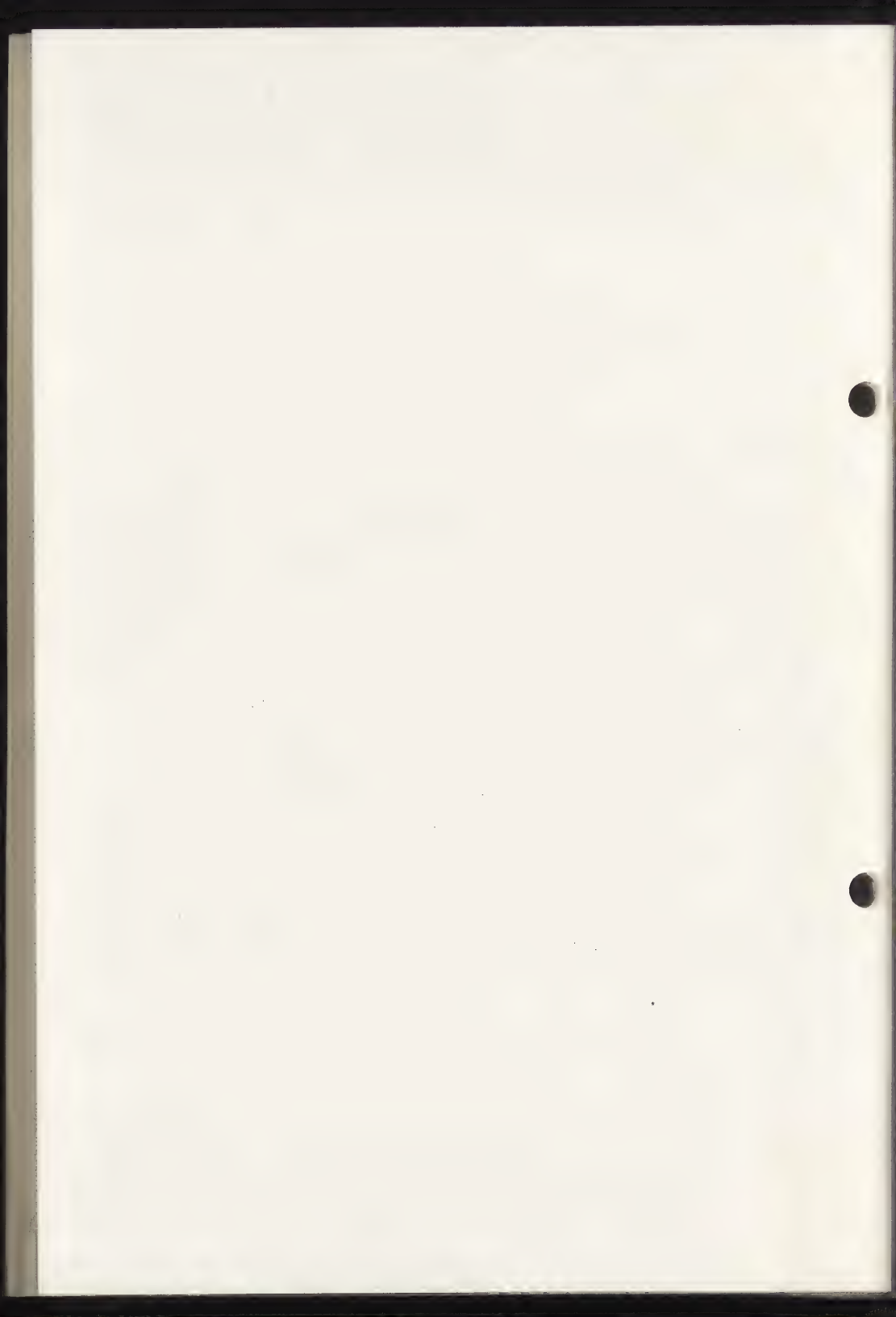
The back of the leather was cleaned only dry. I had to remove the glue and starch layers in some places. While it was the starch that kept together the leather and the wooden board, the glue went onto the leather as result of a previous intermediary repairing.

The softening may only be made after mounting the leather from the grain-side with a special watery (likker) emulsion.

The last phase of the preparation of the leather for mounting was the thinning down of the edges of the parts to be completed.

The complementing of the gaps will be made on the boards and the gaps being on the book spine will be completed on the saddle itself. (Here a considerable completion was needed both at the head and the foot.) For complementing an indifferent, artificially tanned pig-parchment is used the colour of which is near to that of the cleaned original binding, but it is much thinner as the original leather. It was just for this reason that, in order to reach the original thickness on the edges of the board, on the corners and in general on the meeting points of the old and complemented surfaces, I put a piece of goat of natural vegetable tanning under this pig-parchment. The complementings were pasted on with wheat starch mixed with nipagin and methylcellulose, respectively the pig-parchment was stuck with this adhesive to the goat, and finally the original leather was fixed to the wooden board, that is to these complementings.

In the last phase of the work I prepared the snaps which were then placed on the book-boards.



81/14/15

THE RESTAURATION OF LITHUANIAN FOLK GRAPHIC
WORKS OF ART AND THE INVESTIGATION OF BORATE
BUFFER INFLUENCE ON COLOUR FASTNESS

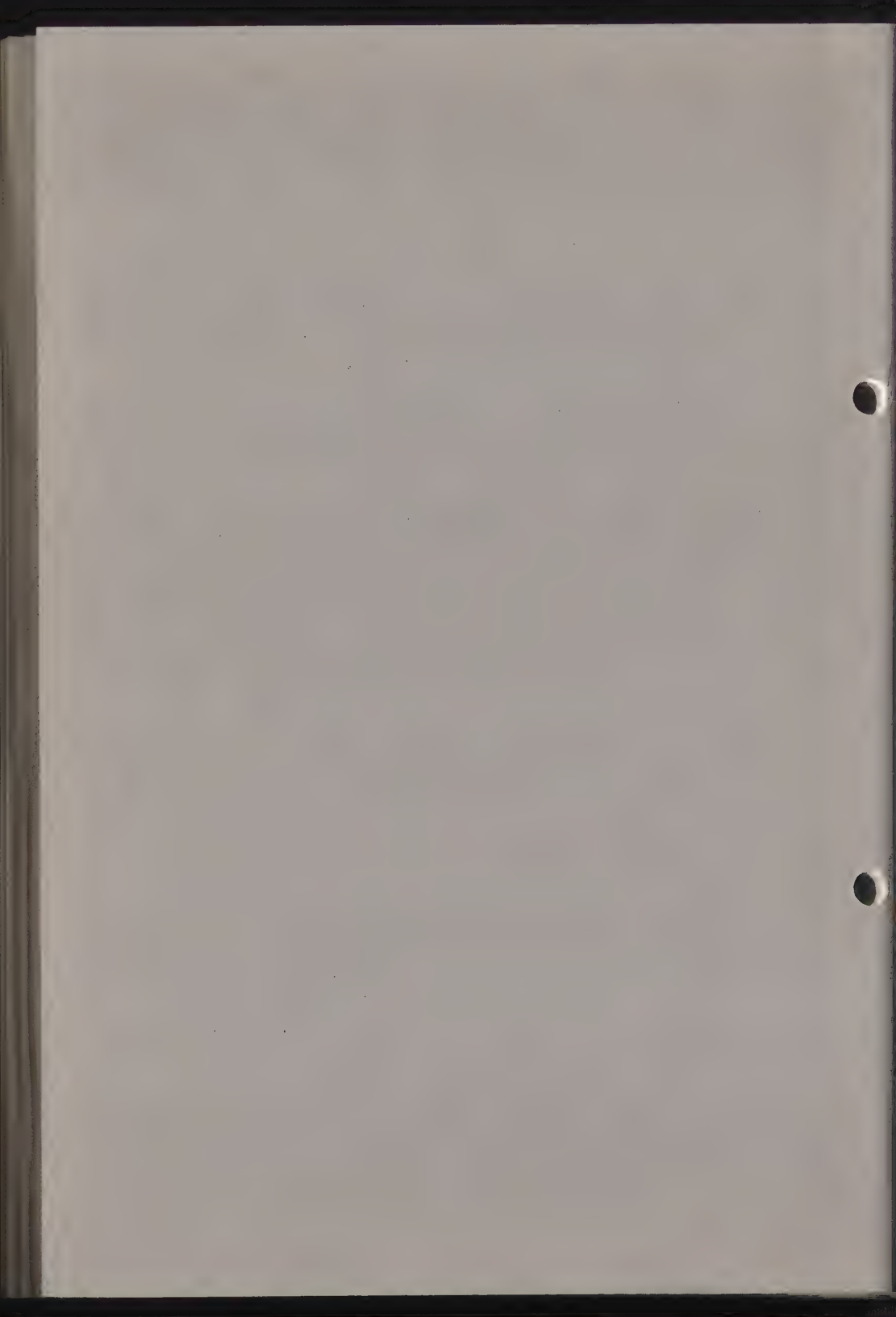
N. Murelytė, L. Vedrickienė and J. Vaitkus

ICOM Committee for Conservation

6th Triennial Meeting

Ottawa 1981

Working Group: Graphic and Photographic
Documents



THE RESTAURATION OF LITHUANIAN FOLK GRAPHIC WORKS OF ART
AND THE INVESTIGATION OF BORATE BUFFER INFLUENCE ON
COLOUR FASTNESS

N.Murelytė, L. Vedrickienė and J. Vaitkus

Art Museum of Lithuanian SSR
The Restauration Centre of Art Treasures named after
P. Gudynas
55 Gorky Street
Vilnius, Lithuanian SSR 232024
USSR

The report acquaints with original graphic prints of the folk artists of Lithuania of the 19th century and with their restoration. The technological analysis of the prints is presented. The investigations of the possibility to use borate buffer for the neutralization of paper of the coloured prints are described. A new method of reconstructing great losses of pieces of graphics is presented.

Introduction

Graphic prints of folk artists occupy a special place in the Lithuanian folk art and in the cultural heritage of the Lithuanian people. They are original coloured xylographs mostly on religious plots.

At the end of the 19th- at the beginning of the 20th centuries folk graphic art and painting were ousted by manufactured printed pictures-oleographs brought from Germany. Out of fashion works were not being preserved- they were stored in sheds and garrets. (1)

Large collections of folk graphic prints, in most cases badly damaged and not suitable for preserving and exposing were gathered in the museums of Lithuania by means of systematic expeditions to the villages.

The restoration of the collected folk graphic works was begun in the Graphic Department of the Restoration Centre of Art Treasures named after P.Gudynas at the Lithuanian Art Museum. There have already been restored over a hundred of badly damaged pieces of graphics. The aim of the authors of the report is to acquaint with the fulfilled investigations and with practical restoration of the graphic works of folk artists.

The technological analysis of xylographs

The graphic art of folk artists is original and peculiar by its execution technique. Soft lime wood most often served as the material for xylographic plates. The plate was ground, then coated with chalk or wax to make easy superimpose picture with a pencil, a pen or a brush.

There are two typical sizes of xylographs: a little one-an impression from one plate and a large one- from 4-5 plates. The printed fragments are sloppily stuck together, therefore the picture of separate parts of a xylograph often doesn't coincide.

Original is the colouring of impressions: dyes were stencilled with little brushes. Not more than three-four colours were used in painting. It is interesting

that often one and the same composition variant has different colouring.

It was corroborated by the chemical analysis of the works under restoration that the paint media had been prepared on glues of carbohydrate or protein origin. In order to achieve lustre or to intensify brightness of colour the painted layer used to be covered with egg glair.

The set of pigments used by folk artists is not great: yellow and brown ochre, raddle, minium, yellow chrome, the Prussian blue, indigo, ultramarine, the Veronese green.

It was elucidated by means of paper composition analysis that paper of different kinds was used: from manually moulded ragpaper to factory made out of wood-pulp. Separate fragments of xylographs of large sizes were stuck together by flour glue.

The state before restoration

The received for restoration sheets of prints were badly damaged mechanically, in some cases they were with great losses of image, made dirty with soot, dust, excrements that covered a bright colouring of the printed layer. the measuring of pH of the paper showed strongly increased acidity- up to 4.8 what, apparently, conditioned fragility and ageing of the paper support.

Investigations

In connection with the restoration of coloured folk

graphic prints with rather increased acidity investigations of the borate buffer - a neutralizing means - on the process of dye ageing were carried out. The aim of the work is to explain the possibility of using the borate buffer that is widely and successfully applied by us for the paper of documents and black-white graphic prints in the case of works executed in colours.

Experimental . Experiments were carried out with experimental pieces painted with water-colour dyes. Investigations were carried out with the following pigments: ferric oxide, zink white, the Naples yellow, green oxide or chromium, cobalt , cadmium pigments , ultramarine, the Prussian blue , a number of organic pigments . The dyes were superimposed on the experimental clippings of water-colour paper (pH-5.8) with a soft brush as evenly as possible. For control samples dyes were diluted in water. Paintings of experimental samples were being made on the paper worked out with buffer mixture pH of which 7.5 till reaching the limit pH meaning of 6.8 (2) Dyes were diluted with the buffer as well.

The ageing of the dyes was being modelled by irradiation with a mercury-quartz lamp [PK-2 at the distance of 0.5 m. Exposure to irradiation was being carried out for about 60 hours. The temperature of the samples reached 30° C.

Before and after the irradiation spectrophotometric curves of the reflection of dyes on the spectrophotometer

C Φ -10 were read. Little quantity of binding material allowed to interpret the data as the change in optical characteristic of pigments.

Data processing. Calculations were carried out in the following way: under a determined length of the wave corresponding to the maxima of changes of the spectral curve was calculated relative reflection deviation-value $\frac{\Delta T}{T_0}$, where T_0 - reflection coefficient of not radiated sample, T - reflection coefficient of the same sample after irradiation. An error was assumed to be 0.5 % of deviation under minimum reflection (10 %) .

As the paintings were done by hand 3 samples of every colour were prepared and average value $\frac{\Delta T}{T_0}$ was calculated.

Comparative evaluation of relative reflection deviations on control and experimental paintings was carried out. The data are presented in the table:

Pigment	$\frac{\Delta T}{T_0} \cdot 10^{-2}$		Nature of changes	
	Control	Sample with buffer		
1	2	3	4	
Chinese White	0	0	-	
Ivory Black	+ 5,25	+ 6.95	440nm 660 nm	-
	- 1,45 440 nm 660 nm	- 3.33		
Ultramarine	+ 4.0	+ 4,0	470 nm 660 nm	stabilization
	- 8,5 470 nm 660 nm	- 1,5		
Cobalt Blue	+ 5,17	+ 4,1	440 nm 560 nm	-
	- 1,53 440 nm 560 nm	- 4,0		

1	2	3	4
Prussian Blue	+6.85 -14.8	460 nm +5,3 660 nm -32,5	460 nm 660 nm Fading
Green oxide of Chromium	+6,6	440 nm +8,73	440 nm -
Naples Yellow	4,9	440 nm 3,25	440 nm -
Cadmium Yellow	14,95	440 nm 14,07	440 nm -
Cadmium Lemon Yellow	0	-10,7	440 nm Fading
Raddle	-2,5 -1,5	500 nm -8,33 640 nm -2,37	500 nm 640 nm Fading
Raw Sienna	-5,0 -0,47	500 nm -1,5 640 nm 2,35	500 nm 640 nm -
Indian Yeallow	-0,16	460 nm 0,23	460 nm -
Carmine	-20,85 -1,55	500 nm -9,5 620 nm 1,8	500 nm 620 nm Stabi-
Madder Lake	-10,75 -2,3	520 nm -2,33 600 nm -0,2	520 nm 600 nm "
Thioindigo	-7,1 -23,8 -2,6	440 nm -4,3 540 nm -9,23 640 nm -2,4	440 nm 540 nm 640 nm "

Discussion of results . Processing with the borate buffer has some influence on the colour fastness of pigments. (In majority of cases positive: colour fastness doesn't change or increase.) The Prussian blue on the buffered samples is less fast to light irradiation than on the control paintings. An insignificant fading of cadmium lemon yellow and raddle take place but in the range of spectra not determining the colour of the given pigments.

Variation and fastness of pigments between the control

and experimental samples partially depends on the paper pH difference. It is known that photochemical reactions taking place on the hard basis are complex. The full analysis of the above mentioned cases requires a separate study.

Taking into consideration the data of investigations, the positive properties of the borate buffer-its simplicity of preparation, its almost neutral pH, fungistatic properties, it was decided to apply the borate buffer for the conservation of paper of painted works after the chemical analysis of the paint layer reservedly approaching the processing of those with the Prussian blue.

Practical restoration

The process of restoration of xylographs consisted of the following stages:

1. Dry mechanical cleaning
2. Removal of stains by compounds selecting them according to supposed stain origin.
3. Washing by plugging up with 0.5 % solution of gelatine in distilled water combining the fixation of colours with washing up to constant pH of the paper.
4. Bleaching of some high quality papers with 3 % solution of chloramine B by the semi-drying method from the reverse side.
5. Processing of papers with pH 5.5-5.8 after washing and bleaching with the borate buffer (pH 7.5) instead of

glycerine water for damping paper under flattening the sheet.

In some cases the processing with the buffer was carried out by multiple sprinkling from the reverse side. pH of the paper increased up to 6.2- 6.8. pH of the paper of the xylographs with the Prussian blue in the paint layer didn't exceed 6.0.

6. The lining of xylographs with extensively damaged paper on equally fast very thin paper of the best quality with wheat-flour glue including sodium floride as antiseptics.

A special lining method was applied for the xylograph "Madonna of the Saint Date " (the author is A.Vinkus) that preserved only about 2/3 of the image in separate fragments. With an experimental aim, fragments were being lined on the copy reproduced with a copying machine from the xylograph identical to the composition of the original work. Fragments under restoration were stuck on the corresponding places of the black-white copy.

A xylograph lined in this way helps to perceive the work of art as a whole what is important under exhibiting.

Conclusions

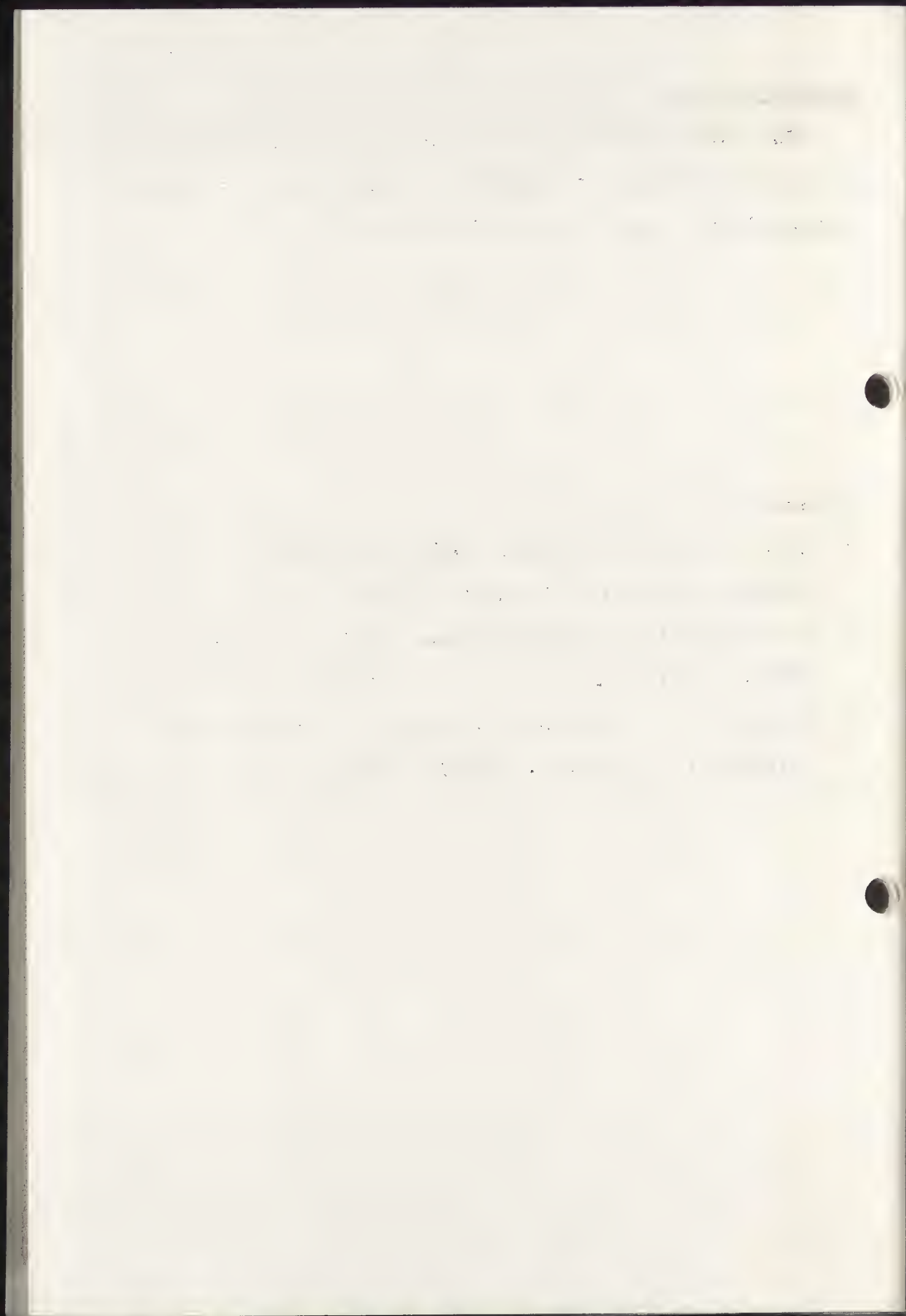
As a result of the carried out work about one hundred pieces of folk graphic prints were restored: paper was fastened and conserved, original colouring was revived and paint layer fastened. They became suitable for storing

and exhibiting.

The investigation data of the borate buffer influence on colour fastness of pigments is applicable for other cases of art works' restoration as well.

Literature:

1. Lietuvių liaudies menas. Grafika ir tapyba.
Sudarė P. Galaunė . Vilnius . 1968.
2. P. Rudniewski, A. Wawarzeńczak . Wpływ niektórych środków neutralizujących na własności papieru.
3. Belenkij E.F., Riskin I.V. Chimiya i technologiiya pigmentov. Leningrad. "Chimya" 1974.



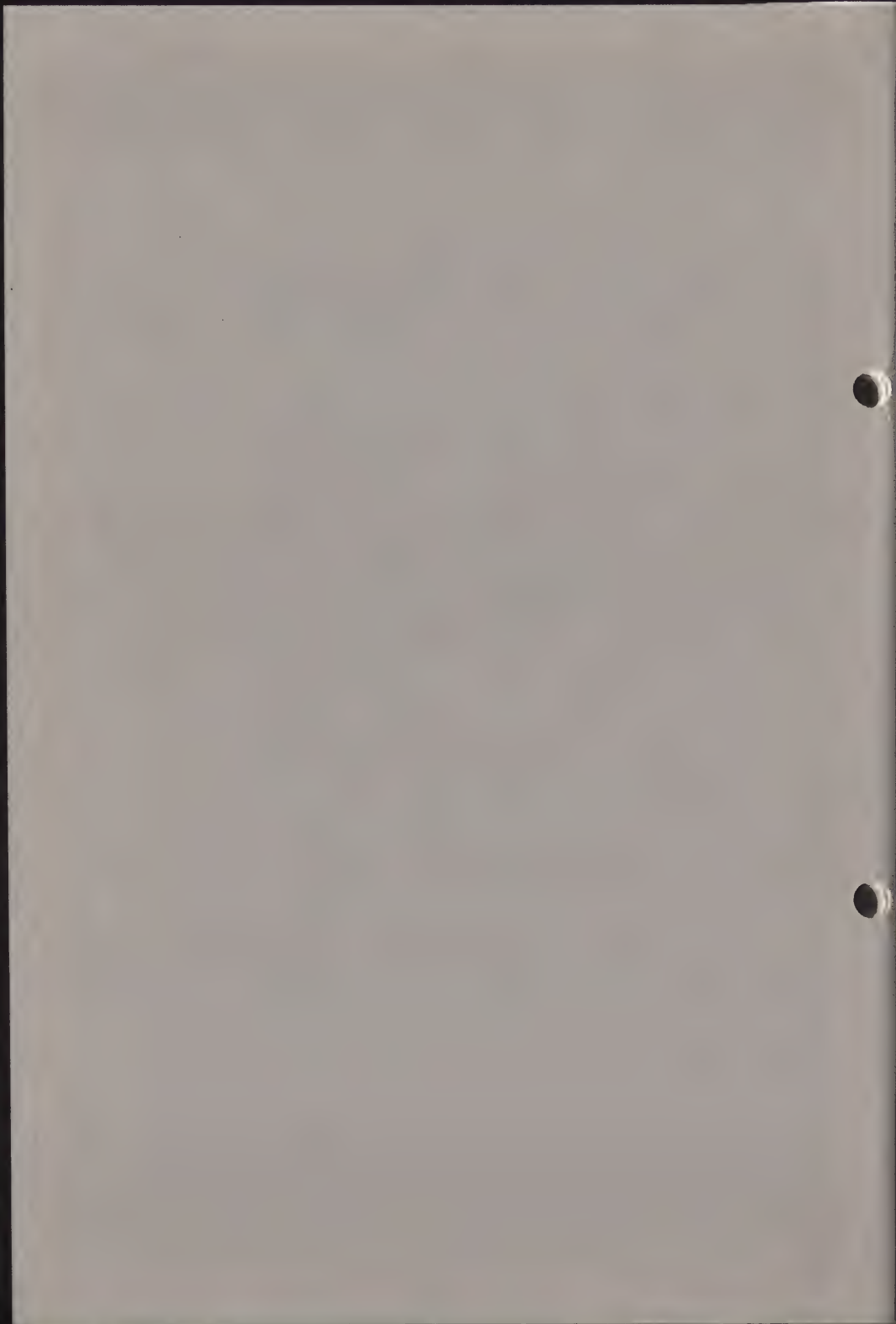
81/14/16

LA RESTAURATION DES PAPIERS CALQUES AUX
ARCHIVES NATIONALES

Christiane Sauçois

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Documents graphiques et
photographiques



LA RESTAURATION DES PAPIERS CALQUES AUX ARCHIVES NATIONALES

Christiane Sauçois

Atelier de Restauration des Archives Nationales
60, rue des Francs-Bourgeois
75141 Paris Cedex 03
France

Résumé.

Depuis plusieurs années, l'atelier de restauration des Archives Nationales utilise les polyamides comme procédé de renfort des documents. Ces matériaux ont l'avantage de conférer une résistance considérable et une très grande souplesse aux documents les plus cassants. A partir de ces constatations, nous avons appliqué ce procédé à la restauration des calques. La méthode de désacidification est choisie en fonction de l'insolubilité des encres et du degré d'acidité du document. Pour le cas précis d'un calque du 18ème siècle, nous avons utilisé le métoxyde de magnésium.

* *

La Section Outre-mer a confié au Service de la Restauration des Archives Nationales un document très endommagé, sur calque, le 13 novembre 1980.

Il s'agit d'un plan coté F³288 n° 40 : intitulé "Plan figuratif de l'habitation sucrerie de Messire Dubuc Duferret située à la Trinité isle Martinique". Echelle 1/4670. Dressé en février 1787 par De La Corbière, arpenteur général et grand voyer, signé de lui. Avec cartouche, rose des vents, légende. C'est un dessin à la plume aqua-réliné. Dimensions : 0,96 m x 0,63 m. Le document avait été relié avec d'autres plans en recueil factice, intitulé "Atlas des Colonies", constitué par l'érudit Moreau de Saint-Méry (1750-1819). Cet atlas en très mauvais état a dû être dérelié de façon à remettre à plat les plans qui s'y trouvaient et dont les grandes dimensions avaient obligé le relieur à les plier. Le n° 40, sur calque, a particulièrement souffert de cette situation et se trouvait en morceaux inutilisables pour un chercheur. M. Jean-Marie Leguay, ingénieur agronome, a entrepris, avec la collaboration de Melle Nathalie Leguay, une étude sur la commune de la Trinité (Martinique) du XVIIe. siècle à nos jours. Il souhaitait vivement consulter ce plan qui avait été retiré de la communication. Le travail très délicat de restauration de ce document va enfin permettre de l'utiliser pour un travail historique. La famille Dubuc-Duferret est l'une des plus anciennes de la Martinique, puisque son fondateur Pierre Dubuc, compagnon de Belain d'Esnambuc, arriva en 1635 en cette île où il fonda des sucreries à Saint-Pierre et à la Trinité.

Les Archives Nationales de France possèdent une importante collection de calques dont la communication pose des problèmes. Ces documents se détruisent d'eux-mêmes et lorsqu'un lecteur doit travailler sur l'une de ces pièces, nous recevons dans nos ateliers de véritables puzzles à reconstituer.

La restauration d'un calque du 18ème siècle, sur papier vergé, nous donne l'occasion d'aborder deux sujets : celui de l'utilisation des polyamides comme renfort des documents et celui de la déontologie en matière de restauration.

Les calques ne peuvent être, à priori, considérés comme de simples copies. Ce sont des documents d'archives et ils constituent parfois le seul élément de travail pour les chercheurs, les originaux n'existant plus, n'étant plus communicables ou étant conservés dans des dépôts lointains. Le plan dont nous allons parler appartient à la première catégorie.

Il s'agit d'un calque dessiné et peint sur un vergé huilé. Le document présente un brunissement ayant comme conséquences une diminution de la transparence et une atténuation de certaines couleurs. L'extrême fragilité du support a entraîné de nombreuses cassures ; des fragments ont été perdus et les détériorations augmentent à chaque manipulation. La mesure du PH indique 4,30. A partir de ce constat le restaurateur envisage les opérations susceptibles d'être appliquées :

- Mise à plat du calque après passage en humidificateur
- Nettoyage à l'aide de pinceaux très fins
- Choix d'une méthode de désacidification
- Choix d'un procédé de renfort
- Reconstitution du plan et comblage des lacunes sur table lumineuse
- Doublage final par thermocollage.

Les opérations de désacidification et de renfort sont choisies en fonction de l'état du document, de son caractère historique, artistique, de la fréquence de sa consultation, etc... La phase théorique étant définie, c'est dans la phase pratique que vont surgir les difficultés. Elles sont de deux sortes : l'une est le lot quotidien du restaurateur et tient au degré de détérioration du document. L'autre tient à la nature même du document; ce dernier devant être sauvé comme document d'archives, même s'il n'a plus la nature d'un calque. De toutes façons, ce choix sera résolu par la triumvirat habituel : scientifique, conservateur, restaurateur.

Nous avons vu que la cause principale de détérioration est une acidité excessive entraînant des ruptures de la chaîne cellulosique. Les buts recherchés sont donc :

- A) De supprimer cette acidité par une désacidification adéquate qui apportera la réserve alcaline la meilleure.
- B) De corriger l'extrême fragilité du document en le renforçant avec un support transparent, neutre et souple, ce qui permettra les manipulations même les plus maladroites sans qu'il y ait de risques de fragmentation ou de déchirures.

C'est donc en fonction de ces critères que nous avons choisi d'abord la désacidification au métoxyde de magnésium sur les conseils du Centre de Recherche sur la conservation des documents graphiques et ensuite le doublage avec polyamides.

Après des essais ponctuels sur différentes parties du calque pour vérifier l'insolubilité de l'encre des textes et des couleurs, nous avons déposé un fragment du document dans un bain de méthanol et de Fréon 113 (trifluorotrichloroéthane) à 50 % pendant 10 mn. Après séchage, la parcelle de document avait perdu un peu de sa transparence mais s'était considérablement éclaircie.

L'alternative était alors la suivante :

- 1) Prolonger la durée de vie de ce plan unique par une désacidification correcte en détruisant partiellement le caractère original et fonctionnel du calque.
- 2) Conserver l'aspect et le caractère particuliers du support en laissant l'acidité faire oeuvre de destruction et rendre à court terme le travail de restaurateur inutile.

Nous avons donc soumis ce problème de fond du conservateur qui, au dernier ressort, avait seul pouvoir de décision. La première solution fut adoptée.

La désacidification a été effectuée en deux phases. (1).

1) Trempage préalable :

Le document mis entre des treillis en fibre de verre a été immergé dans une solution de méthanol et de Fréon 113 à 50 % pendant 10 mn pour dissoudre les acides gras responsables, en partie, du brunissement du plan.

2) Trempage dans la solution désacidifiante :

Le plan a été plongé dans une solution constituée de 500 ml de carbonate de méthyl-magnésium obtenue en faisant barboter dans une solution de méthoxyde de magnésium du gaz carbonique pendant deux heures au débit de 1l/mn. Le plan reste dans la solution jusqu'à absorption à peu près complète de celle-ci. Nous avons obtenu un PH de 9,30.

Procédé de renfort :

Le renfort du verso a été constitué par un tissu polyamide nylon (appellation commerciale Cérex) et par un tissu polyamide thermocollant (appellation commerciale Bifix) sur lequel on a placé le document. L'ensemble a été posé sur une boîte lumineuse, chaque fragment a été remplacé et fixé à l'aide d'un appareil à pyrogravure. Les lacunes ont été comblées par découpe au scalpel, d'un vergé très fin, teinté à la chicorée. Un bifix et une mousseline de soie ont été appliquées sur le recto. Le plan se trouve en sandwich entre deux tissus polyamides thermocollants et deux tissus de renfort, l'un étant un nylon, l'autre une mousseline de soie.

(1). Ces travaux ont été effectués en collaboration avec le Centre de Recherche sur la Conservation des Documents Graphiques.

Conclusions.

L'utilisation des polyamides pour la restauration des calques, appliquée aux Archives Nationales depuis quelques années donne d'excellents résultats et correspond aux besoins exprimés par les conservateurs. Les calques sur vergé posent des problèmes spécifiques inhérents à la nature du support parfois difficiles à résoudre. Il n'existe pas à proprement parler de déontologie en matière de restauration des documents graphiques d'archives. Certaines règles sont établies et restent impératives, ce sont les principes de réversibilité, la permanence des matériaux, la lisibilité, le respect du texte ou du dessin, s'il s'agit de cartes et plans (ne rien ôter, ne rien ajouter). Etablissement d'une fiche technique. Pour les autres principes énoncés dans la littérature cela reste des éventualités non des devoirs. La diversité des objets d'archives, leurs caractères propres, rendent difficiles l'établissement d'un code régissant toute intervention. Chaque pièce doit être considérée avec un soin particulier. Le document d'archive est une preuve d'un moment historique, politique, économique, géographique, etc... d'un pays, cela implique que toutes les connaissances relatives à ce document soient réunies pour sa sauvegarde. D'où la politique de restauration que les Archives Nationales appliquent de façon systématique : la liaison permanente et le travail en collaboration du conservateur, du scientifique et du restaurateur ; dans ce cas particulier ils ont choisi de sauver le document d'archives sans conserver sa nature fonctionnelle de calque.

Nous remercions pour leur collaboration :

Mme Pouliquen, conservateur à la Section Outre-Mer

Mme Leclerc, ingénieur chimiste du Centre de recherche sur la conservation des documents graphiques

Mme Delavaud, restauratrice-spécialiste à l'Atelier de restauration des Archives nationales

Mme Thomasse, photographe de l'Atelier de photographie des Archives nationales

Photo n° 1 - Reconstitution du plan

Photo n° 2 - Fixation d'une pièce de comblage

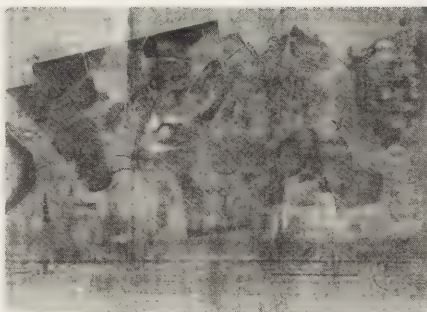
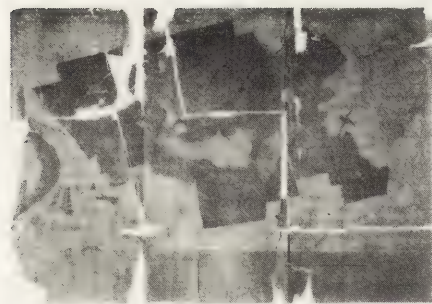
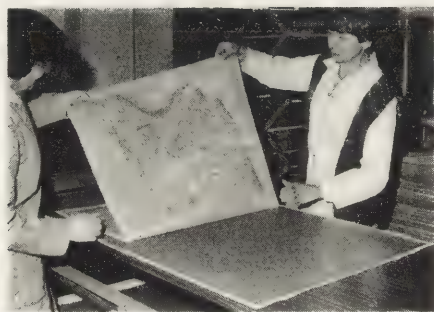
Photo n° 3 - Découpe au scalpel

Photo n° 4 - Levée de l'excédent de papier de comblage

Photo n° 5 - Passage en machine

Photo n° 6 - Plan avant restauration

Photo n° 7 - Plan restauré





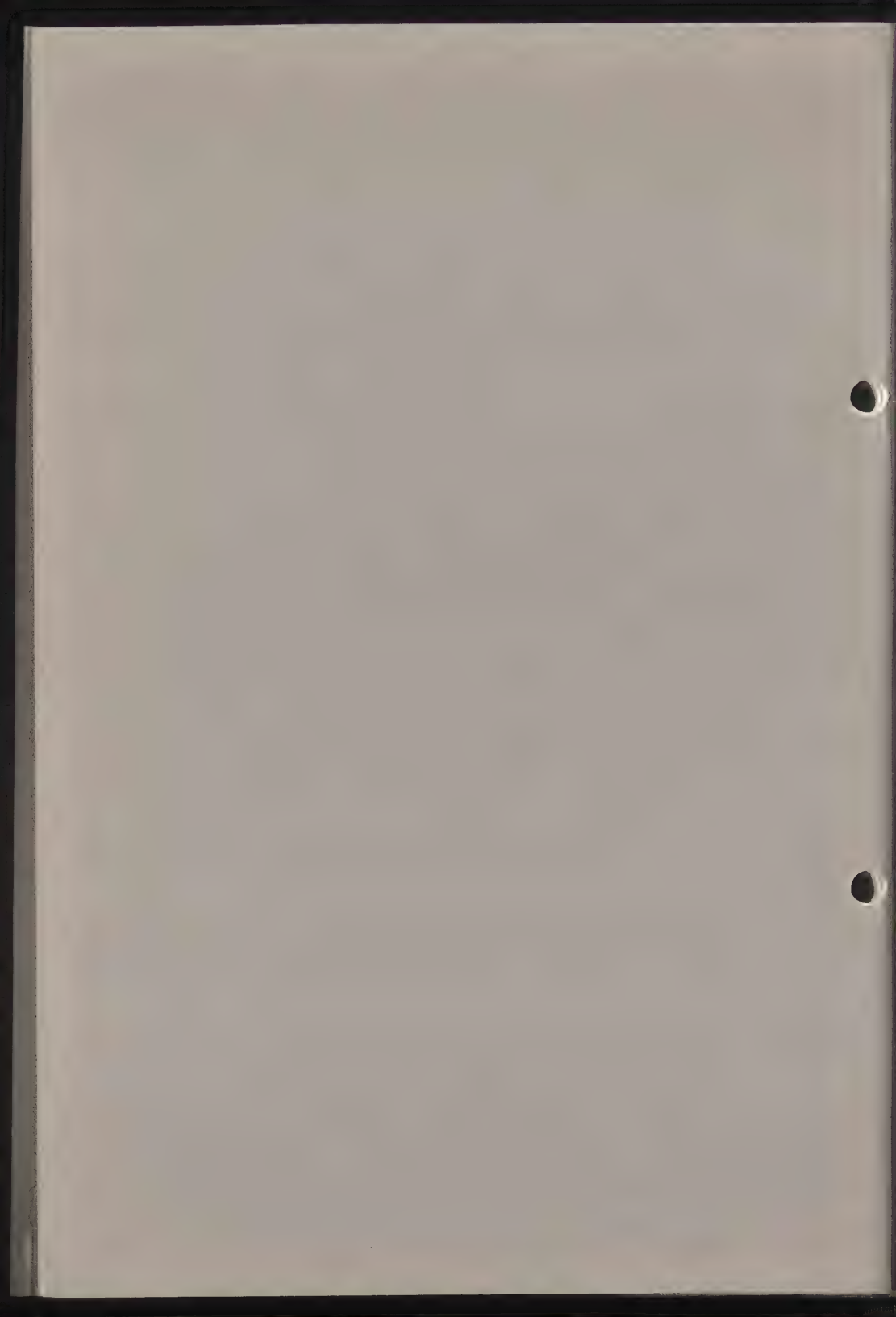
81/14/17

PROBLEMS OF PRESERVATION OF PALM-LEAF
MANUSCRIPTS

O.P.Agrawal

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



PROBLEMS OF PRESERVATION OF PALM-LEAF MANUSCRIPTS

O.P.Agrawal

National Research Laboratory for Conservation of
Cultural Property
C-257, Nirala Nagar
Lucknow 226007
India

ABSTRACT

Palm-leaf has been a popular writing material in Asian countries. A study has been undertaken to know the varieties of palm-leaves used. The results of a survey of processes used for making the palm-leaf fit for writing are mentioned. In some countries like Thailand, palm-leaf was decorated before being written upon. Deterioration of palm-leaf is discussed and future programme of research mentioned.

INTRODUCTION

For several centuries, palm-leaf was a very popular support for writing and painting in India and in other South and Southeast Asian countries like Nepal, Sri Lanka, Burma, Thailand, Indonesia, Malaysia, Kampuchea, and so on. Large collections of palm-leaf manuscripts are found in museums and private collection of these countries. The palm-leaf continued to be used even after paper was introduced because paper remained costly and even today for certain ritual and religious purposes it is used in some parts of India, Sri Lanka, Thailand, etc.

There are many species of palm trees growing in tropical countries. However, the leaves of all of them were not found suitable for writing. It is only a few which were used. A study has been undertaken to know what were the species of leaves used. So far, we have come across the following varieties :

1. *Borassus Flabellifer* Linn (the palmyra palm)
2. *Corypha Umbraculifera* Linn (Talipot palm or Fan palm)
3. *Corypha Taliera* Roxb

BORASSUS FLABELLIFER LINN

Originally a native of tropical Africa, palmyra palm now grows in many parts of India, Burma and Sri Lanka. The tree, it is found, attains a height of 15 to 20 metres. The leaf stalks can be upto one metre. The study of manuscripts show that the palmyra palm-leaves lose their flexibility with age. Initially they are strong and flexible. Also, it is seen that the palmyra palm-leaves are rather thick in comparison to those of talipot palm. Insects attack the leaves of palmyra palm more easily than they do the talipot palm-leaves.

CORYPHA UMBRACULIFERA LINN

The talipot palm grows to a height of 20 to 25 metres. As compared to the palmyra palm it needs a wet climate and, therefore, grows abundantly in areas near to the sea. It is also found in the forests of Sri Lanka, Burma, Thailand, Indonesia and South India. The leaves of the talipot palm are soft and flexible. Moreover, they remain flexible for a longer period. In commerce, the leaves are used for making fans, umbrellas, baskets, roofings, and so on.

CORYPHA TALIERA ROXB

Corypha Taliera Roxb leaves are slightly brown in colour with black spines. The tree goes to a height of about 10 metres and grows mostly in Bengal (India) and some coastal areas of South India. The leaves are not very flexible and are rather thick. They are also easily attacked by insects.

The study is continuing to see if other varieties of palms were also used for manuscripts.

PROCESSING OF PALM-LEAVES

As it would be of interest to know what were the processes used for preparing the palm-leaf for making them fit for writing. A survey was undertaken to collect information about these processes. It is observed that there are several techniques used. The main are as follows :

1. In South India, fresh leaves were first of all dried in the shade and then an oil (gingili oil) was applied on the surface. The oil was allowed to steep in and then the excess was removed with brush.

2. In some parts of South India, fresh palm-leaves are hung in a kitchen so that smoke is deposited on them. Later on they are cleaned and polished with cloth to make them fit for writing.

3. In Orissa, a state in the eastern part of India, palm-leaves meant for writing are hung in the kitchen for a few days and then are cleaned. Later on turmeric paste is applied on them.

4. There is another method prevalent in Orissa. The leaves after being completely dried in the sun are kept under the mud or the silt of the pond. They are removed, cleaned and dried again in the sun. Later on a turmeric paste is applied.

5. In some parts of India, rough and matured leaves are boiled in water for some time to make them thin and pliable. Afterwards, they are cleaned with soft cloth. They are kept alternately in sun and dew for a few days. Sometimes turmeric paste was applied on the surface after the leaves were dry.

6. In Sri Lanka, the fresh young palm-leaves were boiled in water for a few hours. Sometimes lime water was used. The leaves were then dried in shade.

7. In Thailand, the leaves are first dried in the shade. Their ribs are removed with a sharp tool. They are then cut to a uniform size and bundles of its leaves are put between two wooden boards. They are then processed in a heated kiln. The leaves fastened together in heavy wooden boards are kept inside the kiln for approximately 24 hours. At the end, it is found that a black resinous substance comes out of the leaf and is deposited on the sides of the bundle. The black exudation is removed with a cloth. After opening the bundles each leaf is cleaned.

DECORATIONS ON PALM-LEAF

A survey was undertaken to be able to know whether any type of decoration or coloration was applied on the palm-leaf after their processing and before writing. In India no decorations or colour was found to be applied on the palm-leaf except the occasional application of turmeric paste.

In Sri Lanka also the leaves are not decorated or coloured in any manner.

The situation is different in Thailand. There the leaves are coloured and decorated in several ways. A study undertaken some-time back indicates that leaves were variously coloured red, black or blue. On such leaves writing was done with gold ink, particularly on red. White ink which is prepared by mixing a white pigment like chalk with gum is also used. Black lacquer has often been used for colouring palm-leaves. The lacquer is applied evenly on the surface and then the writing was done with gold. Red lacquer was also sometimes used for application on leaf.

In Thailand, white, black and red inks were used for writing on palm-leaf. Gold has also been used profusely. Some examples were seen where the palm-leaf was first gilded completely and then writing was done with black lacquer.

In Burma, the colouring of palm-leaf was not very popular. However, in some cases it was prepared by coating with lacquer of amber colour and then the writing was also done with lacquer of the same colour but of a deeper shade.

A practice very popular in Thailand is the gilding or colouring of the edges of the palm-leaves with lacquer mixed with gold powder or vermillion. This traditional practice serves two purposes - binding the fibres of the palm-leaf edges and saving them from getting soiled.

METHODS OF WRITING AND PAINTING

There were two main techniques for writing on palm-leaf :
(i) by incising with a pointed iron stylus and (ii) by writing with a pen or a brush as is done on paper.

When the writing is done with the stylus the cuts in the palm-leaf are not legible without the application of black. Lamp-black or charcoal powder mixed with an oil is therefore applied on the leaf to make it visible. In India, mustard oil or gingily oil is used for mixing the black. We have come across examples where instead of lamp-black, fresh green leaves are rubbed on the palm-leaf so that the writing becomes legible. Whenever they become illegible, the leaves are rubbed again. A very interesting material used for this purpose is a paste prepared by mixing the juice of the leaves of the plants of a bean (dolichos lablab), eclipta alba, the juice of datura fastuosa, turmeric, black ashes and gingili oil. As will be seen, datura fastuosa is poisonous and may have been incorporated in this paste to impart insecticidal properties.

DETERIORATION OF PALM-LEAF

With time several defects are noticed in palm-leaves. The main are :

- (i) Discoloration : leaves become brown and sometimes black. The main cause of this defect seems to be the oxidation of leafy matter.
- (ii) Stickiness : It is found that certain types of palm-leaf have a sticky surface. This could have been because of the frequent use of oil.

- (iii) Loss of strength : It is seen that the palm-leaf which is flexible when fresh loses its suppleness with age.
- (iv) Biodeterioration : The palm-leaf is easily damaged by insects. It was found that the only insect which could feed on them was gastrallus indicus. It is a tiny insect making holes through the leaves and breaking them into pieces. Fungus is not commonly seen to grow on palm-leaf.
- (v) Stains : Dirt and stains of various types can also be present.
- (vi) Splits in the surface : Horizontal splits on the surface of the palm-leaf are often noticed. The splits are undoubtedly because of the shrinkage of the leaf surface. They can be dangerous in the case of surface-written or surface-painted leaves.
- (vii) Cleavage of surface layers : Yet another defect noticed in the palm-leaf is the separation of the surface layers from the other parts of the leaf.
- (viii) Weakening of edges : The edges of the palm-leaf particularly become fragile. Sometime they get broken even by the slightest touch. The structure of the leaf which otherwise is well-knit starts getting loose at the edges.
- (ix) Fading of ink : If the ink which is filled in the incisions of the writing is lost, the writing becomes invisible. This is a very common defect.
- (x) Flaking of pigments : In case of painted leaves, flaking of pigment is generally present. This may happen because of the loss of the binding medium of the paint or because of the expansion and contraction of the leaf with the climatic changes.
- (xi) In the case of lacquered palm-leaf, the lacquer flakes off frequently.

SOME INVESTIGATIONS

In order to understand the properties of palm-leaf certain investigations were undertaken.

SOLUBILITY OF PALM-LEAF

Experiments were conducted to know what portion of palm-leaf is soluble in different organic solvents.

The following are the results :

Acetone	:	2.25%
Chloroform	:	1.80%
Ethyl alcohol	:	3.5%
Xylene	:	2.8%

The solubility in organic solvents is because of the dissolution of some amount of resin or wax present in the leaf.

ABSORPTION OF MOISTURE

A portion of palm-leaf was placed in a closed cabinet with relative humidity 85 to 90%, temperature 17°C. The leaf was taken out after 24 hours and weight was taken. There was an increase of 3.3% in the weight.

ABSORPTION OF WATER

A piece of palm-leaf was kept in distilled water at room temperature (21°C). It was taken out after 15 seconds and dried between blotting papers. Its weight was taken. It was again placed in water and taken out after 5 minutes. After again blotting, the weight was taken. In this way the weights were taken after every five minutes of being kept in water. It was noticed that the absorption of moisture reached its peak after about 10 minutes. The results are as follows :

Table I

Rate of Absorption of water by palm-leaf

Time	% absorption
15 seconds	Nil
2 minutes	4.9%
5 minutes	9.1%
10 minutes	16.3%
15 minutes	16.3%
20 minutes	16.3%

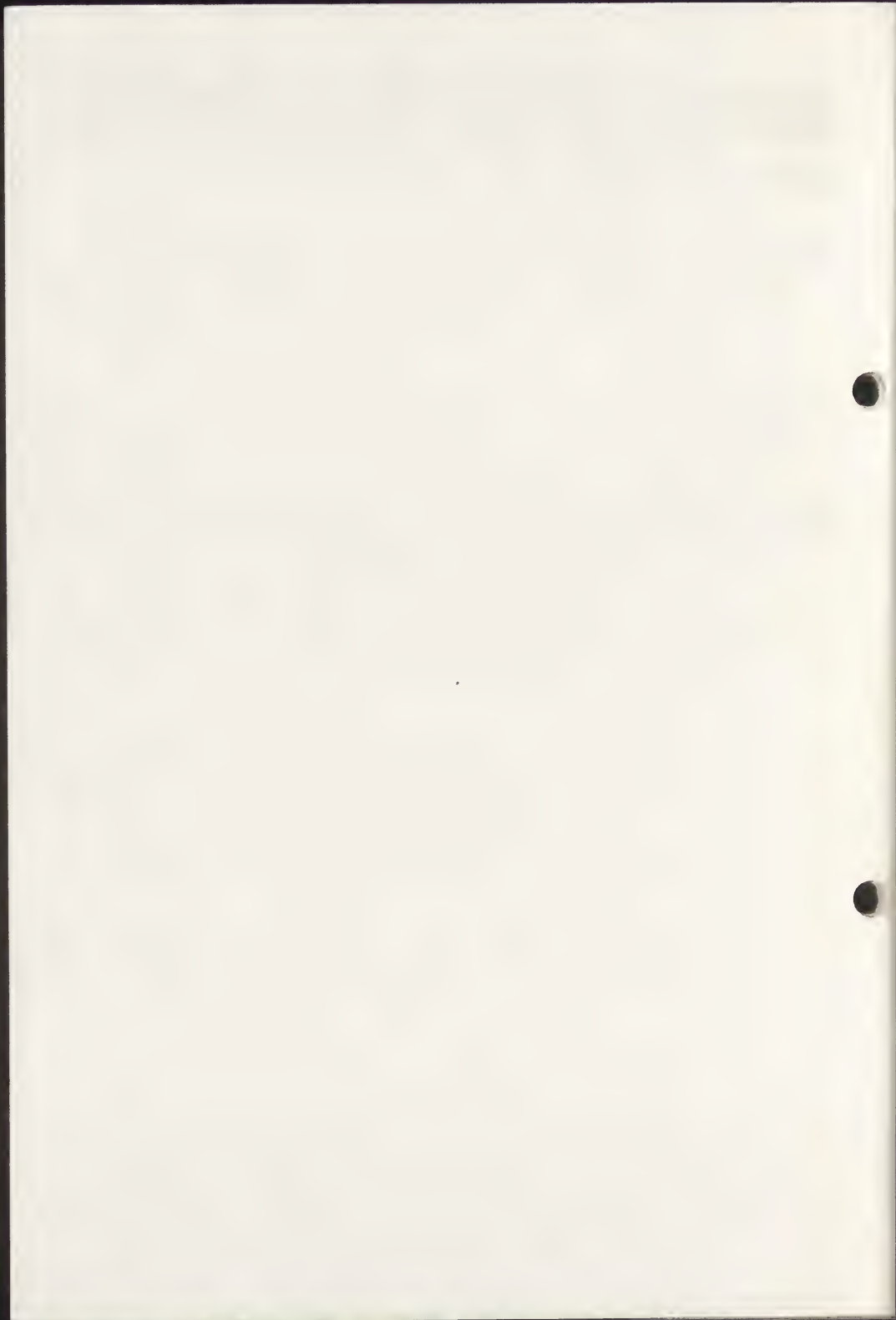
This indicates that if the palm-leaf is wiped clean with swabs of distilled water without dipping it in the solution for a long period, there is not much likelihood of damage.

FLEXIBILITY OF PALM-LEAVES

Experiments are being conducted by using various types of oils to see if they impart flexibility to the leaf. According to a survey, the main oils used in different regions are :

- (i) Citronella oil
- (ii) Camphor oil
- (iii) Gingili oil
- (iv) Dummela oil

The leaf seems to be more flexible for a while, but the effect with lapse of time and the evaluation of their respective effects is yet to be done.



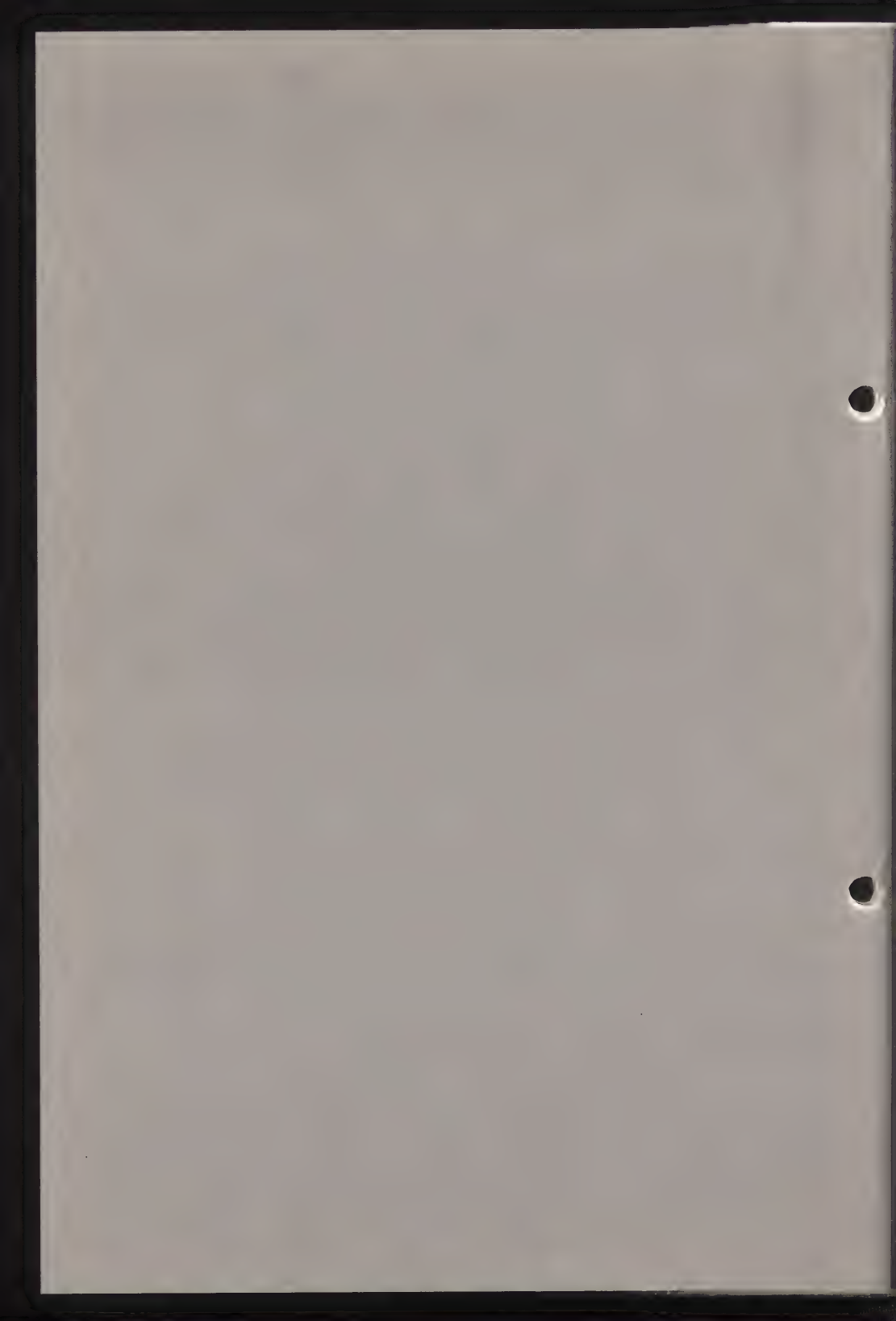
81/14/18

INVESTIGATIONS FOR PRESERVATION OF BIRCH
BARK MANUSCRIPTS

O.P.Agrawal and S.K.Bhatia

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



INVESTIGATIONS FOR PRESERVATION OF BIRCH BARK MANUSCRIPTS

O.P.Agrawal and S.K.BhatiaNational Research Laboratory for Conservation of Cultural
Property

C-257, Nirala Nagar

Lucknow 226007

India

ABSTRACT

Besides palm-leaf, birch bark was another material very commonly used in ancient India for writing. The birch bark is composed of several layers. The layers which remain joined with natural gum and with knots present in the bark start separating. This phenomenon presents a problem in preservation. There is also a weakening of bark material. Some basic properties of birch bark have been studied. The major problems for the preservation of birch bark manuscripts are mentioned.

INTRODUCTION

In India, before the advent of paper sometime in the 12th century, the material used for writing, besides the palm-leaf, was birch bark (bhoj patra). Most of the early birch bark manuscripts, like the palm-leaf manuscripts, have also been destroyed. However, from the accounts available in the literature we find that the birch bark was used for writing since very early time. The Greek historian, Q. Curtius mentions the use of birch bark for writing. He says that the Hindus at the time of Alexander's invasion used the bark of birch tree as writing material. The use of birch bark for writing continued till the Mughal period and for some purposes is used even today. Bhoj patra which is supposed to be a sacred material is used for very religious books as well as for writing sacred mantras which are kept folded within amulets or lockets. People wear these amulets on their arms or around neck for good luck. Alberuni, an Arabic traveller and historian, who came to India during the Mughal period gives a detailed description of the use of birch bark. He describes the process in the following words :

"In central and Northern India people use this bark of the

Tuz tree, one kind of which is used as a cover for bow. It is called Bhurja. They take a piece one yard long and as broad as outstretched fingers of the hand, or somewhat less and prepare it in various ways. They oil and polish it so as to make it hard and smooth and then they write on it. The proper order of the single leaves is marked by numbers. The whole book is wrapped up in a piece of cloth and fastened between two tablets of the same size. Such a book is called Punthi. Their letters and whatever else they have to write, they write on the bark of Tuz-tree."

Birch bark is still widely used in Jammu and Kashmir. There are found large collections of manuscripts in Kashmiri houses.

The birch is a moderate sized deciduous tree growing at an altitude of about 14000 feet (4600 metres) in the Himalayas. It was the inner bark of the tree which was used for writing. It was slowly dried and then oil was applied over it and was polished. The leaves were cut to size, and like in palm-leaf, holes were pierced in the centre, to allow a cord to pass through and hold them together. There were two wooden covers around which the cord was wrapped.

DETERIORATION

The birch bark is composed of several layers, each of which is very thin almost like a tissue paper. It is normally of a very light teak brown colour on one side and brownish white on the other. The layers are joined together by a natural gum and by knots and streaks which are composite parts of the bark. In course of time, and possibly with the effect of moisture, the individual layers of the bark start separating from each other. Also, the material of the sheets deteriorates. The ink used was Indian black, a carbon ink, and was, therefore, fast. However, when the leaves rub against each other, ink also gets abraded.

The birch bark weakens considerably with time. The sheets become stiff and brittle. Gradually they disintegrate.

Insects normally do not have a liking for birch bark.

DIFFICULTIES IN PRESERVATION

It is very difficult to deal with separation of birch bark layers. It is so because of the knots which are present in the bark. These knots are joined together firmly and do not allow the application of an adhesive uniformly to all parts of the sheet, even if a thin brush was used. If an attempt is made to separate the leaves completely, there will be a likelihood of breakage at the spots where the knots are present.

Removal of stains is also difficult because the use of any solution is likely to affect the colour of the sheet.

The birch bark is often conserved between two sheets of glass. However, this technique is not feasible with big collections. Lamination between cellulose acetate foils after acidification of the bark sheets is also recommended. It is the only remedy currently available but the cellulose acetate foil remains adhered to the outermost layers. The inner layers even then can be separated at some stage.

INVESTIGATIONS ON BASIC PROPERTIES

1. Average basic weight (of 3 layers) : 160 gm./sq.mt.
2. No. of nodes in sheets : 1600 per sq.mt.
3. Ash formation : 42% at 950°C
4. Absorption of moisture : 1.4% at R.H.37%;
Temp.35°C
4.4% at R.H.86%;
Temp.35°C
5. Colour of nodes : Deep brown
6. Colour of background : Light buff
7. Fluorescence : Background appear
sky blue
Nodes appear reddish
violet
8. pH : Hot water
extract 6.74
Cold water
extract 6.9
9. Solubilities in various solvents : Xylene - 13.2%
Chloroform - 20%
Acetone - 15.3%
Ethyl alcohol - 13.1%
Water - Nil
10. Elemental analysis : Iron - 4.7%
Nickel - absent

	Copper	- absent
	Sodium	- 0.32%
	Potassium	- 0.2%
	Nitrogen	- Present
	Sulphur	- absent
	Phosphorous	- absent
	Hologens	- absent
11. Copper Number	: Fresh Bark	: 3.9 to 4.3
12. Cellulose content	: α cellulose	: 81.8%
	β + γ cellulose	: 18.2%
13. Starch	: absent	
14. Proteins	: present	
15. Rosin	: present	

MAJOR PROBLEMS

1. Search for a material for impregnation so that the layers are bound together, without losing flexibility, colour and other properties.

2. Reason for apparent insect repellent property. This will enable avoidance of treatment processes which might destroy this property.

3. Restoration of flexibility.

4. Techniques for removal of stains.

Work on above lines is continuing at the National Research Laboratory for Conservation of Cultural Property, Lucknow.

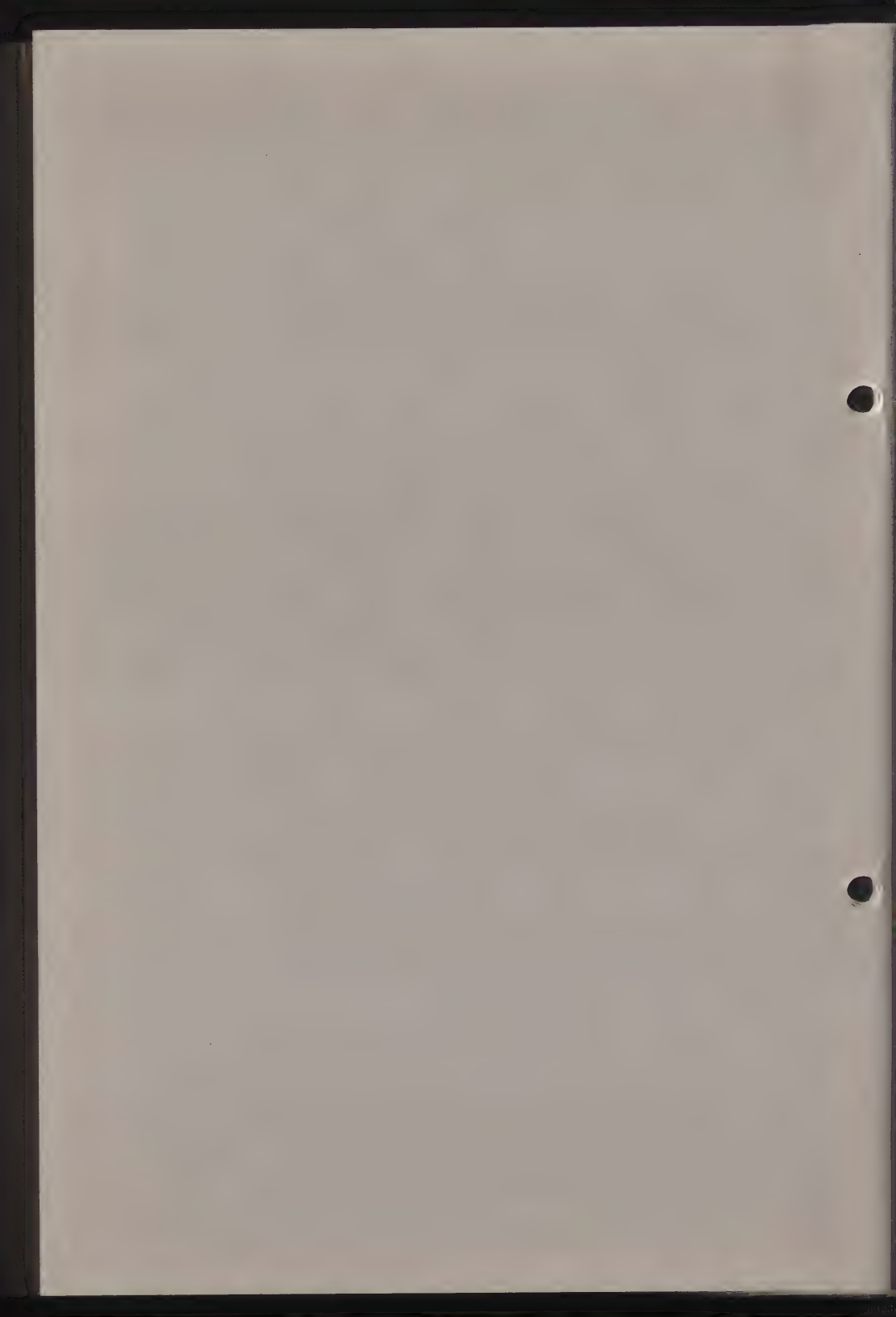
81/14/19

CONSERVATION AND RESTORATION OF LINOLEUM
PRINTING BLOCKS

Jiří Čejka

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group : Graphic and Photographic
Documents



CONSERVATION AND RESTORATION OF LINOLEUM PRINTING BLOCKS

Jiří Čejka

National Museum - Natural History Museum
Research Chemistry Division
115 79 Praha 1
CSSR

A b s t r a c t

A simple method for the treatment (conservation and restoration) of linoleum printing blocks has been described. The treatment consists of following operations:

- a) cleaning (ethanol, containing 2% of petrol)
- b) antimicrobial preservation (vacuum impregnation, 5% ethanol solution of Lastanox Universal)
- c) petrification, fixation on textile bed, vacuum impregnation (acrylate lacquer KP 709)
- d) silicone oil impregnation.

The model experiments have been described. Detailed description of the treatment of Josef Čapek's linoleum printing block (linoleum engraving of the title page of John Barrow's book "Vzpousta na lodi Bounty" 1929) has been given.

All processes for the conservation and restoration of the linoleum printing blocks have been modified in such a way that they could be realised in each laboratory serving for conservation.

I n t r o d u c t i o n

Literature dealing with the treatment, conservation or restoration of printing blocks has been very unnumerous as yet. The references cover rather possibilities how to apply individual conservation techniques. The more detailed working procedures, however, have not been described. Our previous paper / ČEJKA 1975 / was dealt with the treatment of zinc and partly of copper printing blocks in detail. This work concerns the treatment of linoleum printing blocks.

A procedure was effected for conservation and restoration of a linoleum printing block of Josef Čapek (the title page of John Barrow's book: The mutiny on the board Bounty, Czech translation by Jiřina Jílovská and Jan Čep, editor Václav Petr, Praha 1929) after the examination of conservation and petrification materials was carried out.

We worked with specimens of regular already employed about 50 years old linoleum in model experiments because we were not able to obtain a special linoleum for block printing preparation. Patterns of linoleum (size about 1x3 cm) were prepared. The patterns were impregnated in vacuum (by a water jet pump) by a lacquer. We applied two kinds of the lacquer for the petrification of the linoleum, produced by Research Institute for Synthetic Resins and Lacquers in Pardubice / SVOBODA 1976 / :

- a)acrylate lacquer KP 709 - It becomes dry by physical procedure, it is plastified in order to get elastic coating with the high resistance to water and atmosphere. High resistance to turn yellow it is its advantage. It can be used even for the fixation of basis. It is diluted by toluene or xylene.
- b)developing type of acrylate lacquer - It has similar properties in the main as lacquer mentioned above. It provides coatings more elastic.

E x p e r i m e n t a l

Preliminary orientational experiments prove both lacquers, they can be used with success. Therefore, we carried out successive experiments with the aim of determination the optimum concentration of the lacquer and /or whether a successive double impregnation (at first more diluted and then more concentrated xylene solution of lacquer) is suitable. The vacuum impregnation lasted always 30 minutes. The finished experiments proved the results of the preliminary research and confirmed that both acrylate lacquers are suitable with the volume ratio as follows:

Lacquer KP 709 - with regard to strength (tested only by mechanical bending) and appearance (no or negligible gloss), the lacquer to xylene ratios 1:10, 1:7, 1:5 (for the single impregnation) and 1:10 + 1:7 (for the double impregnation). Higher concentration of the lacquer can be used, however, a new suitable treatment of the surface applying an opacifier (e.g. Airosil) would be necessary. Glossy spots may occur even after the double impregnation considered above.

Developing acrylate lacquer - the lacquer to xylene ratios 1:10 to 1:3 (single impregnation), 1:10 + 1:7 to 1:3 + 1:2 (double impregnation). The higher lacquer concentration results in the glossy surface too. Their application is not possible without the use of opacifier.

We used relatively well accessible KP 709 lacquer for the treatment of linoleum printing block made by Josef Čapek. Its application in the museum preservation of collection objects was already well verified as yet by the use to other kinds of material (esp. textiles). The lacquer offers high guarantee even for the long stability and to numerous effects of destruction. The KP lacquer was developed as an adhesive of glass in optics so that the adhesiveness of lacquer is possible to utilise too.

Treatment of the linoleum printing block of J. Čapek
(Instructions - directions for use)

The working procedure :

- Situation before conservation: the basic printing block, size 14x20 cm, a narrow strip on the upper side of the printing block is broken away with the author's name on it. The strip of linoleum almost desintegrated including fabrics. The corners of the printing block broken, even some edges, some parts in the middle crumbled till to the basic fabrics (the largest destroyed areas: 6x1.5, 2x1 and 1.5x1.5 cm). The base of the printing block frayed out at the edges. The second part of the printing block, deformed, the edges with cracks, size 15x21 cm, different material. The printing block will never be used for printing, only as an exhibited object. The aim and purpose of the printing block treatment is his protection and preservation for future generations with regards to importance of Josef Čapek personality in Czech cultural life.
- The printing block cleaning: at first the blocks were carefully degreased and washed up by the ethanol denaturated by 2% of petrol. The purpose of this treatment was to remove the remaining spots of the paint and terpentine, which was used for the cleaning of printing paints. From the back side of blocks, the remainders of sticked paper were removed. The printing blocks were dried at normal temperature as soon as they were free from impurities (lightly loaded not to be wriggled).

- The protection against microbiological attack and moulds: the printing blocks were vacuum impregnated by the diluted solution of Lastanox in ethanol denaturated by 2% of petrol. The Lastanox Universal in original packing diluted by denaturated ethanol (volume ratio 5:100) was used. The printing blocks were dried at normal temperature.
- The two operations (the printing block cleaning and the protection against microbiological attack and moulds) can be carried out in one joint procedure. There is a possibility to replace the two operations by adding preventive Zn-octoates into the lacquer before its use for vacuum impregnation of linoleum.
- The printing block impregnation (petrification) and the affixing to basic fabrics: the printing blocks were vacuum impregnated by KP lacquer diluted by xylene to 1:10 volume ratio. The back side of printing blocks was varnished three times by original KP 709 lacquer and as soon as the printing blocks were dry, they were stuck to basic fabrics by the concentrated KP 709 lacquer (the lacquer was left for 48 hours opened in order to lower the concentration of the solvent-xylene by spontaneous evaporation). The printing blocks were loaded during the drying procedure to prevent from the strain and deformation (twiggling). The lacquer penetrated to the front side of the printing block at several places. The lacquer was removed by acetone. This measure was necessary to carry out very much carefully because acetone dissolves the original paint of the linoleum.
- The completion of printing blocks: the old linoleum, used for the above described model experiments, was grounded to flour powder, dried and coloured by a brown painting earth. The material, prepared in that way and bonded by concentrated KP 709 lacquer, was used for completion the areas which have fallen out on the face side of printing block (the basic printing block), for the completion of edges, of a gap between the basic printing block and the part of printing block (with the author's name) originally broken away or torn off which was stucked in the same time together with the basic printing block to the common basic fabrics. The remainders of glossy spots were carefully removed by the denaturated ethanol or mechanically. The basic fabrics (made of linen) which was stucked on the back side of printing block, we cut off about 0.5 cm along the edges of printing block.
- The printing block impregnation by silicone oil: both printing blocks were heated in the dry-box to the 70°C (the dry-box was open, only short heating, temperature must not be too high not to start the decomposition of the organic components of printing block) and still warm were impregnated by the 5 vol.% solution of Luko-

oil M 350 in medicinal petrol. The redundant oil was wiped off. (This kind of impregnation by silicone oil is necessary to omit as far as the printing block should be used for printing and make it up for the impregnation by polyurethane lacquer).

- The storage of printing blocks: the printing blocks were inserted into covers from stiff paper to prevent the wriggling and then into a polyethylene cover.

- The applied reagents: denaturated ethanol(2%-petrol)
Lastanox Universal, n.e. Lachema
Brno

KP 709 acrylate lacquer, Res.
Institute of Synthetic Resins
and Lacquers, Pardubice
medicinal petrol
Lukoil M 350, silicone oil,
n.e. Syntézia, Kolín
brown painting earth

D i s c u s s i o n a n d s u m m a r y

A procedure for treatment, conservation and restoration of linoleum printing blocks has been described. Model experiments were carried out which enabled to choose proper concentrations of acrylate lacquers for the petrification of printing blocks. The application of higher concentrated lacquers was also considered. It is possible to prevent the occurrence of glossy surfaces after the adding of an opacifier.

The treatment of the printing block from Josef Čapek, which was based on the results of model experiments, has been described in detail. The printing block was necessary significantly petrificate and affix to the basic fabrics (to avoid the full desintegration of printing blocks). Therefore, we used the original concentrated KP 709 lacquer for the coating of the back side of blocks after the impregnation of blocks by the KP 709 lacquer diluted by xylene to 1:10 volume ratio. In order to enhance the sticking function of the lacquer, it was concentrated by a spontaneous evaporation of the solvent. From the given data, it follows that we must choose the proper concentration of petrifying lacquers according to nature and extent of the damage of printing blocks or according to specified requirements and necessities of the conservator (restorer). The certain disadvantage of higher lacquer concentrations is the formation of glossy surface or glossy spots. It is not difficult to removed the glossy areas nevertheless the working procedure would be complicated. We can prevent it, as mentioned above, by the use of an opacifier. The impregnation of printing blocks by a solution of Lastanox in ethanol is easy and the

applied organostannic compounds fulfil their protective tasks. Also the application of the hydrophobic very resistant silicone oil at the end of the printing block treatment (or of the polyurethane lacquer if the printing block should be used for printing), we consider as quite verified.

The described working procedure is very simple, neither a specified equipment nor chemicals not available are necessary, so that ever conservation laboratory can carry out it easy. It is only necessary to keep the basic safety measures for the work by using vacuum and combustibles.

The author expresses his gratitude to Ing.B.Svoboda, CSc., Research Institute of Synthetic Resins and Lacquers in Pardubice for his interest in this work, for his offer of lacquers to model experiments and discussion about partial issues and to Dr.A.Šilhová and Mrs.E.Kaprálová for their kind cooperation.

R e f e r e n c e s

ČEJKA, J. (1975): A simple method for the conservation of zinc and copper printing blocks. ICOM Comm. Conservation 4th Triennial Meet. Venice, Preprint 75/25/1. 1-9.

KAPRÁLOVÁ, E., ŠILHOVÁ, A., ČEJKA, J. (1979): Contribution to the conservation and restoration of linoleum printing blocks. National Museum in Prague-Natural History Museum, Research Chemistry Division Report, 14pp.

(unpublished report - in Czech); Časopis Národního muzea v Praze, řada přírodovědná, (in press) - in Czech.

SVOBODA, B. (1976): Informace o plastických hmotách vhodných pro muzejní praxi. Přednáška na celostátním semináři muzejních konzervátorů v Dedinkách. (Information on polymer materials and their application in museums. Lecture, all-state conference of museum conservators, Dedinky) - in Czech.

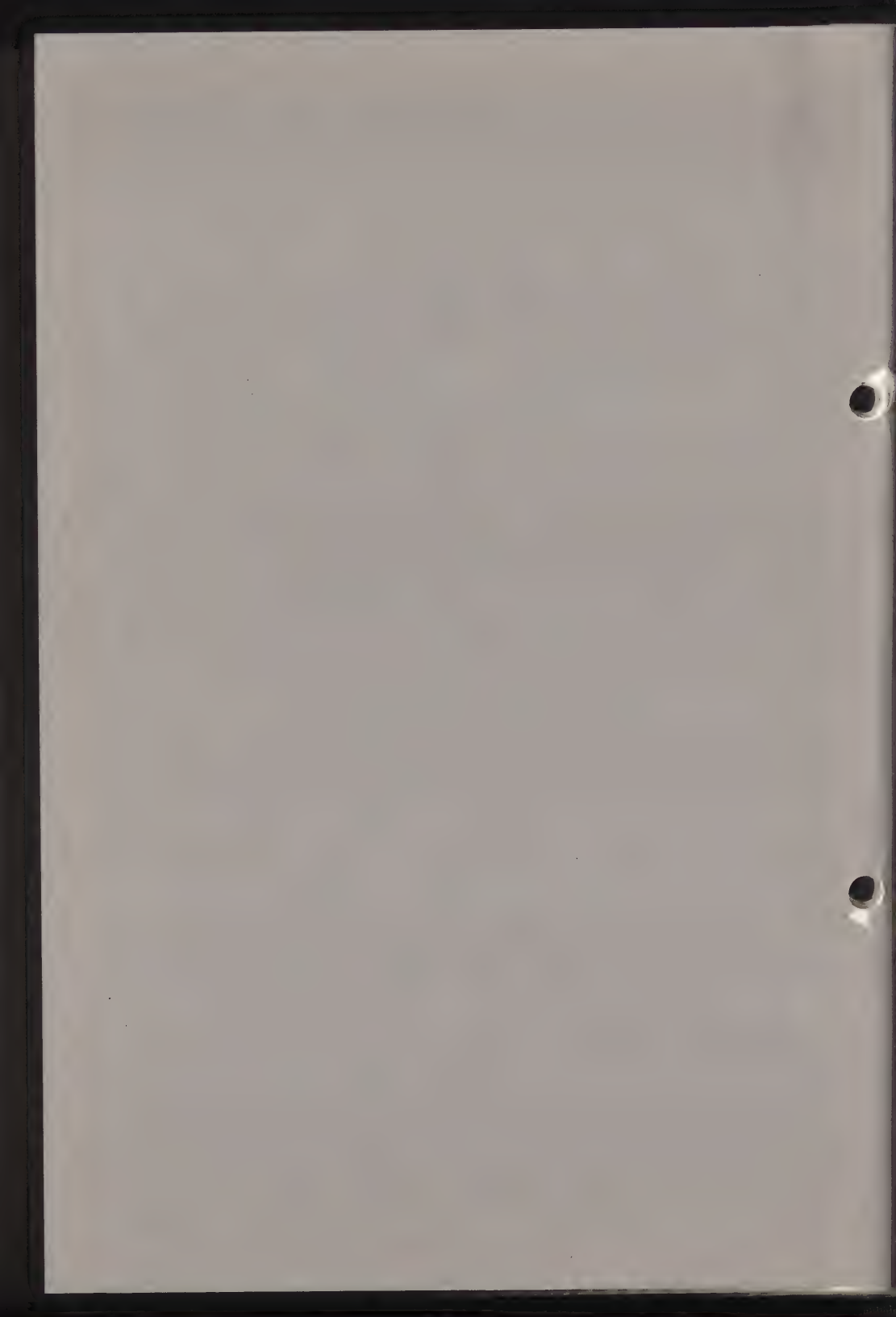
81/14/20

ADVANCES IN THE USE OF HYDROGEN PLASMA FOR
REDUCTION OF SILVER TARNISH.
TREATMENT OF DAGUERROTYPES

V. Daniels

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



ADVANCES IN THE USE OF HYDROGEN PLASMA FOR REDUCTION OF
SILVER TARNISH. TREATMENT OF DAGUERROTYPES

V. Daniels

Department of Conservation and Technical Services
British Museum
London WC1
Great Britain

Advances in the use of Hydrogen Plasma for Reduction of Silver
Tarnish. Treatment of Daguerrotypes.

Abstract

A glow discharge in a low pressure hydrogen will contain chemically active hydrogen capable of reducing silver tarnish (silver sulphide) back to silver. This method has been used to conserve Daguerrotypes which have become tarnished with good results. Previously described methods have been modified so that the Daguerrotype is made one of the electrodes of a low frequency alternating current circuit. Reductions take place using a potential difference of about 400 volts using neon/hydrogen mixtures.

Introduction

Silver sulphide is formed on the surface of bright silver objects because hydrogen sulphide, always present as a pollutant in the air, will react with the silver surface to form silver sulphide. Thin layers of silver sulphide approximately 50 - 500 nm thick display colours due to interference effects, similar to those produced by oil films on water. Thicker layers appear brown or black.

Removal of the unwanted tarnish usually requires the use of chemicals to convert the silver sulphide into soluble compounds, or abrasives which use mechanical action. Some silver polishes use a combination of these two modes of action. Both of these methods involve loss of silver from the object because the silver combined as silver sulphide is removed and perhaps some of the metallic silver.

A method which could be used in some cases is to reduce the silver sulphide back to silver. Previously, the only reducing agent that would do this was hot hydrogen, the object and the gas were being

heated to several hundreds of degrees centigrade before this action proceeded at a satisfactory rate.

One method of activating the hydrogen, so that it will react with the silver sulphide, is to produce a glow discharge in it at low pressure.

Production of Plasmas

When a potential difference of several hundred volts is applied across two electrodes in a gas at a pressure of approximately 13 Pa (0.1 torr), the vessel is filled with a luminous glow. The bulk of the glow adjacent to the anode and stretching to about 25 mm away from the cathode is called the plasma region.

The apparatus used consists of a 300 mm diameter bell jar with a Viton rubber gasket sitting on an aluminium baseplate. Holes in the baseplate are provided for evacuation by an oil diffusion pump with liquid nitrogen trap and for the introduction of terminals to provide an electrical supply to produce the glow discharge. In some experiments we use two pieces of aluminium mesh 120 mm square as the electrodes producing a glow discharge between them by applying a potential difference of about 400v (peak). A gas mixture of 1:1 argon and hydrogen is usually used in the bell jar, at a pressure of about 13 Pa (0.1 torr). Detailed descriptions of this apparatus appear elsewhere (1).

When the glow discharge is produced a lilac coloured glow fills the bell jar but the glow is strongest between the electrodes. On close examination it can be seen that there is a slightly darker region which extends 25 mm around the electrodes. It is the bright part of the discharge which is properly called the plasma region. In the plasma there are free electrons, positive and negative ions of both gases and energetic neutral species. These have high chemical reactivity but are not capable to heating the surface of objects placed in the plasma by more than about ten degrees centigrade. In the plasma silver sulphide at the surface of a silver object can be reduced to silver.

Daguerrotypes

Some silver objects have a surface so delicate that no attempt can be made at polishing and even silver-dip type treatments are regarded with disapproval; the Daguerrotype falls into the category. This process is one of the earlier methods for producing a photographic image and was developed by Louis Daguerre working with J Nicéphore Niepce. The process was made public in 1839 at a meeting of the French Academy of Sciences and Daguerre was subsequently appointed an officer of the Legion of Honour. Daguerre's process involved using a sheet of silver or Sheffield plate (silver on copper). The silver was polished and then sensitized to light by

exposing it to iodine vapour. The plate was exposed in a camera and developed by contact with vapour from a dish of warm mercury. The image was then fixed by immersion in hot sodium chloride or sodium thiosulphate solution. A later development was to increase the sensitivity of the plate up to 100 times by sensitizing first with iodine and then with extra treatments with bromine or chlorine. In 1840 Fizeau invented a gold treatment for Daguerrotypes which improved the contrast but did not otherwise alter the appearance of the plate. This treatment involved immersion in a solution of gold (1) thiosulphate, which deposited gold on the surface of the Daguerrotype (2).

The image on the polished silver surface is made up of tiny granules of silver/mercury amalgam. When the Daguerrotype is viewed in the correct lighting conditions the granules scatter light and areas with a high density of granules appear lighter than other. This gives a positive image of excellent quality.

Finished Daguerrotypes were often mounted in glass fronted frames. Hydrogen sulphide can gain access to the silver surface at the outer edges of the picture. Thus most tarnished Daguerrotypes have their tarnish layer at the outer edges.

Existing Conservation Methods

There are a few methods for the removal of such a tarnish layer. All of them involve dissolving away the silver sulphide while leaving the image intact. The earliest of these techniques, the use of potassium cyanide solution was abandoned because the image could be lost and, besides, the chemicals are highly toxic (3).

The remaining methods use a 'silver dip' type of solution which contains an inorganic acid plus thiourea. The solutions are slower and milder in action than commercial silver dips. One example (4) contains thiourea, a wetting agent and phosphoric acid. Excellent results are often obtained but there are many curators who will not consider the use of such treatments because of the possibility of damaging the image. One danger is that despite thorough washing a trace of thiourea may be left behind and this can cause rapid local retarnishing producing black spots, "Daguerrian measles." (5)

The New Conservation Method

The technique developed is one which has been modified from that previously published (1). The reaction vessel contains only one aluminium mesh electrode the other electrode is the Daguerrotype itself. Electrical contact is made by means of PVC coated wire and a crocodile clip. Making the object an electrode produces more efficient reduction of the silver sulphide because of the greater energy of the particles hitting the surface.

The object is usually placed face upwards in a glass Petri dish and the chamber is evacuated to about one mP. The gas mixture is admitted until the pressure reaches a value of 13 Pa and the voltage is increased until a visible glow is just discernible. The reduction proceeds for a few minutes until the desired level of reduction is obtained.

Experiments using direct current show that most of the reduction occurs when the object is the cathode. The inert gas will form positive ions which are accelerated towards the cathode. If the ions are heavy and have sufficient velocity there is a possibility of silver being knocked off the surface of the cathode. This is known as physical sputtering and may be eliminated by using a lighter inert gas, neon, instead of argon and as low an operating potential as possible.

The layer of silver sulphide reduced to silver is practically invisible and the new silver surface looks highly polished. Thick brown tarnish, however, will produce a milky opalescence on reduction, due to redeposited silver. If the opalescence will obscure the image on a Daguerrotype this method of treatment is not suitable.

Several Daguerrotypes have now been treated using the plasma technique and generally good results have been obtained. If the object should subsequently retarnish there is no reason why plasma reduction cannot be repeated. Experiments on silver test pieces show that this can be done at least four times.

Acknowledgements

I would like to thank Dr M W Pascoe and Professor L Holland for their help and encouragement and Mr N Meeks and Mr P Wilthew for help in the experimental work. I would also like to thank Mr T Collings and F Young for suggesting this use for plasma hydrogen.

References

1. Daniels, V D, Holland, L, and Pascoe, M W, Gas Plasma Reactions for the Conservation of Antiquities. *Studies in Conservation* 24 (1979) 85-92.
2. Swan, A, Fiori, C E, and Heinrich, K F J, Daguerrotypes: A study of the Plates and the Process, *Scanning Electron Microscopy*, 1 (1979) 411 - 423.
3. Swan, A, Conservation Treatments for Photographs, *Image*, 21 (1975) 24 - 31.
4. Collings, T J, and Young, F J, Improvements in some Tests and Techniques in Photograph Conservation, *Studies in Conservation*, 21 (1976) 79 - 84.
5. Pabbravsky, I, Daguerrotype Preservation: The Problem of Tarnish Removal, *Technology and Conservation* 3 (1978) 40 - 45.

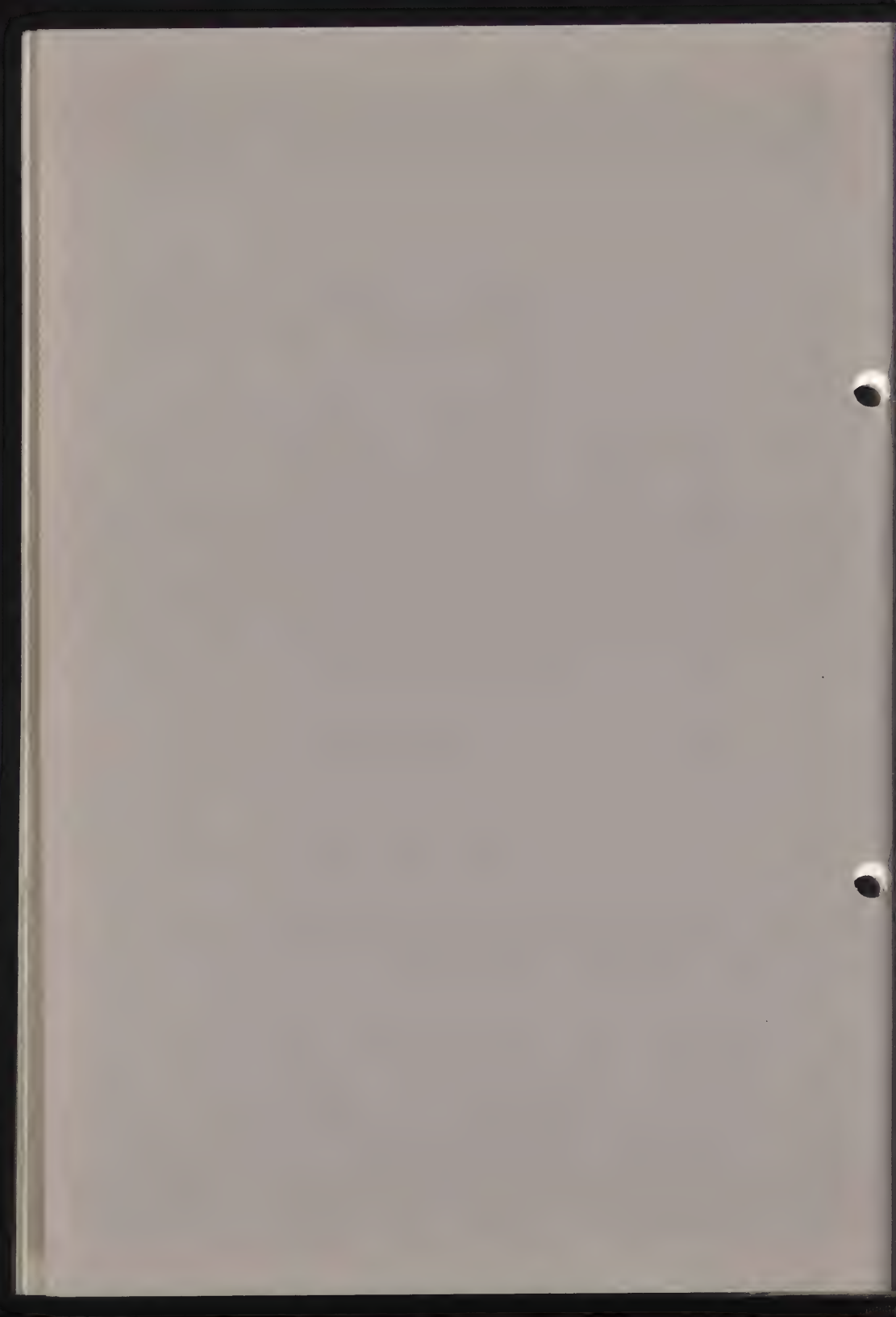


INFLUENCE DE L'ENVIRONNEMENT SUR LA
CONSERVATION DES DOCUMENTS PHOTOGRAPHIQUES
MODERNES

Martine Gillet, Chantal Garnier et
Françoise Flieder

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Documents graphiques et
photographiques



INFLUENCE DE L'ENVIRONNEMENT SUR LA CONSERVATION DES
DOCUMENTS PHOTOGRAPHIQUES MODERNES

Martine Gillet, Chantal Garnier et Françoise Flieder

Centre de Recherches sur la Conservation des Documents
Graphiques
36 Rue Geoffroy-Saint-Hilaire
75005 Paris
France

Résumé

De nombreux produits photographiques noir et blanc et couleur (Films négatifs, positifs et inversibles, épreuves sur papier) ont été soumis à l'action de la chaleur et de l'humidité. Après un an de vieillissement artificiel, il a été possible de classer les échantillons analysés suivant leur stabilité. Les phototypes noir et blanc n'ont pas subi d'altération. Par contre, la dégradation relativement rapide des images couleur a permis de mettre en évidence le rôle plus important de la chaleur par rapport à l'humidité.

Parallèlement des échantillons en couleur ont été exposés à la lumière naturelle. Il est encore trop tôt pour conclure sur les premiers résultats et les recherches sont poursuivies.

La conservation des images argentiques noir et blanc et couleur pose de nombreux problèmes qu'il est indispensable de résoudre pour formuler des conseils aux responsables d'archives. La synthèse des données de la littérature a montré que, si les facteurs de dégradation sont connus, les conditions de conservation ne sont pas toujours précises. Les normes établies pour le fixage et le lavage des phototypes en vue d'un archivage de longue durée sont parfaitement définies (1). Par contre, les conditions thermohygrométriques ne sont pas fixées très exactement en particulier pour les produits couleur : il est conseillé de maintenir une température et une humidité relative basse dans l'aire de stockage des matériaux ; cependant, les auteurs donnent une fourchette trop large surtout pour la température.

Il nous a paru nécessaire de déterminer les conditions thermique et hygrométrique optimales. Nos recherches ont donc porté sur l'étude de l'influence de la température, de l'humidité et de la lumière sur de nombreux phototypes argentiques couramment commercialisés. Elles seront poursuivies ultérieurement sur d'autres procédés (diazotiques, vésiculaires ...). L'ensemble des résultats permettra d'estimer la stabilité des matériaux analysés.

1. DESCRIPTION DE L'EXPERIMENTATION

1.1. Choix des tests de mesure

Les premiers essais ont été faits sur un film Kodak (5234 DNGF). Après avoir expérimenté un grand nombre de tests reflétant la résistance physico-chimique, nous avons conclu que seules les mesures du retrait et de la densité optique de l'image donnaient des résultats significatifs d'une altération. C'est la raison pour laquelle nous avons limité notre travail à l'étude de la variation de ces deux paramètres.

1.2. Choix des échantillons

Afin d'étudier divers types d'émulsions et de supports, nous avons collecté auprès des principaux fabricants de phototypes (Kodak, Agfa, 3 M, Ilford, Fuji) les produits gélatino-argentiques noir et blanc et couleur les plus courants.

La plupart des échantillons couleur sont des procédés à développement chromogène parmi lesquels seul le Kodachrome n'a pas de coupleurs incorporés ; les négatifs ont en plus des coupleurs colorés servant de masque lors du tirage. Nous avons étudié en parallèle trois produits Cibachrome dont le procédé est différent, car l'image est obtenue par destruction de colorants préalablement incorporés dans les différentes couches de gélatine.

Pour les épreuves papier, les fabricants tendent à remplacer le support traditionnel baryté par un produit dit "RC" formé d'une feuille de papier prise en "sandwich" entre deux films de polyéthylène. La stabilité de ce matériau étant très contestée, nous nous sommes penchés sur ce problème et avons choisi d'étudier des échantillons sur les deux types de support. La liste des divers films et papiers examinés figure en annexe.

Ces échantillons nous ont été fournis sous la forme de sensito-grammes, exposés et développés chez les fabricants de façon standard. Ceci nous a permis de mesurer les variations densitométriques dans toute la gamme de sensibilité.

1.3. Choix des conditions d'exposition

D'après les travaux antérieurs, nous savons que les facteurs de dégradation les plus importants sont essentiellement liés aux conditions de traitement et conservation.

Nous ne reviendrons pas sur les causes d'altération dues au mauvais fixage et lavage (thiosulfate résiduel*) qui sont bien connues aujourd'hui et dont nous avons rassemblé les données de la littérature dans une première publication (2).

* La teneur maximale doit être inférieure à $0,7 \mu\text{g}/\text{cm}^2$ pour un archivage de longue durée.

Par contre, nous nous intéresserons aux paramètres de l'environnement jouant un rôle primordial dans la conservation des phototypes, c'est-à-dire : la température, l'humidité, la pollution, la lumière et la nature des contenants.

Nous avons commencé nos recherches en expérimentant la tenue des phototypes noir et blanc et couleur à diverses températures et humidités. Chaque type de produit a été soumis aux conditionnements suivants :

température : 23°C, 35°C, 50°C, 80°C

humidités relatives : 25 %, 40 %, 65 %, 85 %

durées d'exposition : 1 mois, 6 mois, 1 an, 2 ans, 3 ans ...

Les températures ont été choisies volontairement basses, dont une proche de l'ambiance, afin de pouvoir vérifier à longue échéance les extrapolations faites par de nombreux chercheurs (3) à partir de la loi d'Arrhénius pour prédire la durée de vie des phototypes.

Les humidités relatives retenues sont des valeurs couramment observées dans nos régions.

La combinaison des facteurs température-humidité aurait nécessité l'utilisation de nombreuses enceintes climatiques pour conditionner les phototypes que nous avons sélectionnés. Aussi, pour pallier à cette difficulté financièrement insurmontable, nous avons décidé de conditionner chacun des échantillons dans des pochettes étanches aux hygrométries désirées. Ces pochettes (complexe polyéthylène-aluminium-papier) sont ensuite placées dans quatre étuves sèches maintenues aux températures choisies pendant toute la durée d'expérimentation. Pour obtenir le taux d'humidité désiré avec précision à l'intérieur des pochettes, nous avons dû faire un montage spécialement conçu pour cet usage : une boîte à gants dans laquelle on fait circuler l'air à humidité voulue. L'humidité est obtenue en dosant à l'aide de deux débitmètres de l'air sec et de l'air 100 % humide. Ce système permet d'avoir toute la gamme entre 15 et 90 % d'humidité relative. L'expérimentation est réalisée dans une salle climatisée à 23°C et 50 % d'humidité relative où tous les échantillons sont conservés avant et après tout vieillissement. Quelles que soient les expériences réalisées, les mesures sont toujours effectuées après 24 heures de conditionnement dans la salle.

Parallèlement, nous avons exposé les phototypes couleur à la lumière du jour (en plein sud derrière une vitre) de manière à pouvoir étudier leur comportement.

2. RESULTATS

2.1. Méthode d'interprétation

Actuellement, nous avons analysé le comportement de tous les échantillons collectés et vieillis un mois, six mois et un an. Vu le nombre très important de résultats obtenus, il a été nécessaire, pour l'interprétation, d'utiliser un ordinateur (Tektronix 4051) commandant une table traçante.

Nous avons tracé les courbes de noircissement caractéristiques

des émulsions* et calculé les variations (en pourcentage) des densités maximales et minimales pour tous les échantillons vieillis par rapport à leurs témoins. La rétraction du support a également été mesurée.

Pour les phototypes couleur, nous avons fait apparaître la balance des couleurs pour trois éclairagements différents : en pied de courbe, au milieu et à la densité maximale. Afin de pouvoir conclure sur la stabilité des colorants, les variations de densité optique ont été calculées à partir d'une densité initiale de 1,00 (valeur moyenne des zones les plus importantes de l'image) en tenant compte du jaunissement du fond de base. Nous avons noté les variations de densité supérieure à 10 %, seuil d'une dégradation décelable visuellement.

2.2. Action de la température et de l'humidité relative

Les phototypes noir et blanc

Ils n'ont pas subi de variations densitométriques supérieures à 10 % après un an de vieillissement, même aux conditions les plus sévères (50°C, 85 % d'humidité relative). La rétraction du support est restée très faible (0,2 %). Notons que les papiers "RC" se sont aussi bien conservés que les papiers barytés. L'étude est donc poursuivie sur des périodes plus longues (deux ans, trois ans ...) afin de pouvoir déterminer les limites de stabilité de ces matériaux.

Les phototypes couleur

Ils subissent des modifications densitométriques notables et particulièrement le colorant cyan qui se dégrade beaucoup plus rapidement que les deux autres quel que soit l'échantillon (tableau 1). La rétraction du support est aussi faible que celle des phototypes noir et blanc.

Pour les films négatifs, aussi bien l'Eastman Color negative 5247 que le Fujicolor F II, le colorant cyan commence à pâlir à partir de six mois de stockage à 50°C. Les humidités élevées augmentent très légèrement cette dégradation. Le colorant jaune (ou le coupleur coloré) se modifie également après un an à 50°C. Le colorant magenta n'a pas varié.

Les films positifs analysés réagissent très mal à toutes les conditions thermo-hygrométriques auxquelles ils ont été exposés (à l'exception du Cibachrome transparent) : c'est le colorant cyan qui se détériore, les deux autres restant inchangés. La dégradation rapide du Gevacolor print T 986 est accélérée simultanément par des températures et des humidités élevées (notamment à 50°C). Par contre,

* Les courbes représentent les variations des densités optiques en fonction du logarythme de l'éclairement lors de l'impression du sensitogramme.

l'altération des deux films positifs 3M (HP 895 et 3M 881) est indépendante de l'humidité.

Parmi les films inversibles, le Kodachrome 64 possède le meilleur comportement aux températures et humidités considérées. Seul le colorant cyan des films Fuji single 8 et Fujichrome R 100 se dégrade à partir de 6 mois à 50°C ; si, pour le Fuji single 8, l'humidité intervient très peu, pour le Fujichrome elle accélère la réaction.

Les papiers ont en général une bonne résistance aux agressions thermo-hygro-métriques. Ils commencent à s'altérer à partir de 6 mois de conditionnement à 50°C (perte de 10 % atteignant 30 % après un an pour le colorant cyan) quelle que soit l'humidité. Seul l'Agfacolor MCN 310 se dégrade plus rapidement : on remarque déjà une perte de colorant cyan (après un an à 35°C et après 6 mois à 50°C) qui s'accélère avec l'humidité. De plus, il se produit un léger jaunissement (après un an à 50°C) perceptible également sur l'Ektacolor 14 RCF. Le Cibachrome print CCP D 182 et le Cibachrome RC pearl CRC 895 semblent se conserver beaucoup mieux que les autres papiers. Cependant, nous ne pouvons l'affirmer car les résultats sont encore incomplets;

Tous les échantillons soumis à une température de 80°C ont très mal réagi, particulièrement à forte humidité (85 % H.R.) : l'émulsion a collé à la pochette servant au conditionnement ; pour des humidités moyennes (40 % et 65 % H.R.), les produits Cibachrome ont une tenue nettement supérieure à celle des procédés à développement chromogène dont tous les colorants sont altérés.

D'après nos résultats, nous constatons que la température est le facteur de dégradation le plus agressif pour l'ensemble des échantillons analysés. Dans de nombreux cas, l'humidité semble ne pas accélérer l'altération pour des températures inférieures ou égales à 50°C. Cette hypothèse est surprenante car dans toutes les publications concernant la conservation des phototypes couleur, il est spécifié de maintenir une humidité relative faible (30 % au moins) dans l'aire de stockage des matériaux. L'humidité joue cependant un rôle considérable quand la température est élevée (80°C).

Dans la gamme des produits étudiés, le procédé "Cibachrome" possède une stabilité à la chaleur et à l'humidité supérieure à celle des procédés à développement chromogène. Parmi ces derniers, le Kodachrome 64 se montre le plus résistant. Ceci n'est pas surprenant, car les coupleurs ne sont pas incorporés; Roger BELLONE (4) avait déjà observé ce phénomène dans sa collection de 10.000 diapositives archivées depuis vingt ans.

Nous pouvons classer les autres échantillons analysés par ordre de stabilité décroissante : les papiers (exception faite pour l'Agfacolor MCN 310) se comportent assez bien, de même que les films inversibles Fuji (single 8 et Fujichrome). Viennent après les deux négatifs dont la stabilité est mauvaise ; ceci est inquiétant car ces

documents originaux sont destinés à un archivage de longue durée. Les films positifs sont les échantillons les moins stables ; ils se dégradent très rapidement à la chaleur et à l'humidité ; il faut donc les utiliser comme copies d'exploitation et ne pas les archiver.

Malgré ces nombreux essais, nous n'avons pas encore assez de recul pour pouvoir prévoir la durée de vie des phototypes couleur. Nous devons poursuivre les conditionnements sur des périodes plus longues au-delà d'un an.

Nous essaierons d'établir une loi qui régit la dégradation en fonction de tous les paramètres (température, humidité, temps) ; pour ceci, il sera nécessaire d'effectuer des conditionnements à des températures comprises entre 50°C et 80°C.

2.3. Action de la lumière (tableau 2)

Seuls les phototypes couleur ont été soumis à l'action de la lumière naturelle derrière une vitre pendant les trois mois d'été (juillet à septembre). La température de la pièce où ont été exposés les échantillons est restée comprise entre 18°C et 25°C et l'humidité relative entre 40 et 70 %.

Les procédés à développement chromogène

Les films négatifs (Eastman color 5247 et Fujicolor F II) commencent à s'altérer très légèrement après trois mois d'exposition.

Les films positifs se dégradent très rapidement. Après trois mois, les colorants jaune et magenta ont disparu de moitié pour le film 3 M 881 et presque totalement pour le Gevacolor print T 986 ; seul le colorant magenta du film 3 M HP 895 a été détruit, le jaune n'ayant subi qu'une altération de 30 %. Le colorant cyan de tous les films positifs n'est que très peu altéré.

Le film inversible Kodachrome 64 réagit très mal à la lumière naturelle. Ses colorants jaune et magenta disparaissent rapidement : après 51 jours d'exposition, perte de 57 % pour le jaune et 70 % pour le magenta.

Les papiers sont sensibles à la lumière naturelle. Après trois mois d'exposition, la dégradation est peu visible sur l'Ektacolor 74 RCF et le papier 3M. Elle se remarque plus rapidement sur l'Ektachrome 14 RCN (perte de 17 % pour le colorant jaune). L'altération la plus importante est observée sur le Fujicolor (perte de 25 % pour le colorant jaune, de 39 % pour le magenta).

Le procédé Cibachrome : il réagit différemment des procédés à développement chromogène. L'altération ne porte pas sur le colorant jaune mais sur les deux autres ; bien que faible, elle se remarque après trois mois d'exposition (perte de 20 % du colorant cyan et 10 % du magenta).

La lumière naturelle fait virer les procédés à développement chromogène vers le cyan-vert et le Cibachrome vers le rouge.

De nombreux auteurs affirment que le Cibachrome est plus résistant à la lumière que les procédés à développement chromogène (5,6). Les résultats que nous avons obtenus montrent que le papier Ektacolor 74 RCF est aussi stable à la lumière que le Cibachrome. Avant de conclure définitivement, nous devons poursuivre l'expérience.

Le classement des échantillons en fonction de leur stabilité vis-à-vis des variations thermiques et hygrométriques reste valable en ce qui concerne leur comportement à la lumière, à l'exception du Kodachrome 64. Ce dernier relativement stable au noir se dégrade très rapidement à la lumière.

Dans une étude ultérieure, nous examinerons le comportement des échantillons soumis à diverses sources lumineuses artificielles afin de choisir l'éclairage le moins nocif.

o
o o

Nos premières recherches sur la conservation des images argentiques ont permis de préciser les stabilités relatives des divers procédés examinés. Elles ont également confirmé des conclusions déjà énoncées dans la littérature :

Les phototypes noir et blanc n'ont subi aucune altération malgré la sévérité des conditions de vieillissement appliquées.

Parmi les phototypes couleur étudiés, le cibachrome possède la meilleure résistance aux agressions thermo-hygrométriques. Tous les procédés à développement chromogène sont altérés plus ou moins rapidement sous l'action conjuguée de la chaleur et de l'humidité, à l'exception du Kodachrome 64 qui fait preuve d'une grande stabilité.

Cette étude a mis en évidence un fait nouveau concernant le caractère plus nocif de la chaleur par rapport à l'humidité qui n'intervient comme accélérateur de dégradation que pour des températures élevées. Ceci peut conduire à envisager des conditions hygrométriques moins sévères dans les unités d'archivage.

Dans le but de vérifier les hypothèses avancées, les recherches sont poursuivies en utilisant des durées d'exposition plus longues, des températures différentes. Elles seront complétées par le choix du contenant idéal pour une conservation d'archives.

Nos travaux sur la conservation des matériaux photographiques, volontairement limités dans une première étape aux images argentiques, seront étendus aux procédés diazoïques, vésiculaires et électrostatiques. L'expérimentation sera conduite de manière analogue à celle décrite ci-dessus.

BIBLIOGRAPHIE

- (1) "Photographie - Microcopies gélatino-argentiques sur film - Traitement et conservation pour archivage", norme ISO 2803-1974 (F)
- (2) GILLET (M.), FLIEDER (F.), *La conservation des phototypes gélatino-argentiques noir et blanc sur support tri-acétate de cellulose et polyester*, I.C.O.M., Zagreb 1978, 87/14/16
- (3) TUIITE (R.J.), *Image stability in color photography*, Journal of Applied photographic engineering, 1979, vol. 5, n° 4, p. 200-207
- (4) BELLONE (R.), *La conservation des photos en couleur*, Photo-Ciné-Revue, avril 1980, n° 4, p. 192-201
- (5) WILHELM (H.), *Color print instability*, Modern Photography, février 1979, p. 92
- (6) BERMANE (D.), *On the resistance to fading of silver dye bleach transparencies*, The Journal of Photographic Science, 1974, vol. 22, p. 84-92

Nous remercions très sincèrement MM. J. POURADIER et P. BABY (Société KODAK) pour l'aide et les conseils qu'ils nous ont prodigués au cours de ce travail, M. MARTROU (Société KODAK) qui nous a familiarisées avec les méthodes d'interprétation utilisant l'informatique, et tous les représentants d'industries photographiques ayant fourni les échantillons de base pour cette étude.

A N N E X E
LISTE DES ECHANTILLONS TESTES

PHOTOTYPES NOIR ET BLANC

Films négatifs

Kodak 5224 600
Kodak 5231 141
Gevapan 36 T 195

Films positifs

Kodak 5302 263
Agfa T 5.61
3 M - 150

Microfilm

Agfa - copex pan

PapiersBarytès

Kodabrom KG 2 765
Brovira special 112
Guilleminot-Guilbrom
Ilfobrom DW
Ilfobrom SW

"RC"

Kodabrom RCF 2 715
Brovira special 312
Guilleminot plastifié
Ilfospeed (développement machine)
Ilfospeed (développement main)
Ilfospeed multigrade
(développement machine)
Ilfospeed multigrade
(développement main)

PHOTOTYPES COULEUR

*Procédés à développement chromogène*Films négatifs (coupleurs colorés)

Eastman Color Negative 5247
Fujicolor F II

Films positifs de copie (support en tri-acétate de cellulose)

Gevacolor print - type 986
3 M - Color positive HP 895
3 M - Color positive 881

Films inversibles

Fujichrome R 100
Fuji single 8 - F C P 8200
Kodachrome 64 (coupleurs non incorporés)

Papiers

Ektachrome 14 RCN (inversible, surface semi-mate)
Ektachrome 74 RCF (surface brillante)
Fujicolor
3 M - papier couleur
Agfacolor MCN 310

Procédés "cibachrome"

Cibachrome transparent CCT-D 661 (support en polyester)
Cibachrome print CCP-D 182
Cibachrome R C pearl CRC 895

T A B L E A U N ° 1

VARIATION DE LA DENSITE OPTIQUE* DU COLORANT CYAN EN FONCTION DE LA TEMPERATURE, DE L'HUMIDITE ET DE LA DUREE D'EXPOSITION

Echantillons	T°C	25 % H.R.			40 % H.R.			65 % H.R.			85 % H.R.		
		1 mois		12 mois	1 mois		12 mois	1 mois		12 mois	1 mois		12 mois
		6 mois	12 mois	6 mois	12 mois	6 mois	12 mois	6 mois	12 mois	6 mois	12 mois	6 mois	12 mois
FASTMAN COLOR 5247	23	0	- 1	- 2	0	- 1	- 2	0	- 1	- 2	- 3	0	
	35	0	- 3	- 6	0	- 8	- 6	- 2	- 5	- 9	0	- 8	
	50	- 2	- 13	- 25	- 4	- 17	- 25	- 7	- 24	- 38	- 12	- 41	
	80				- 45	- 73		- 75			- 11		
FUJICOLOR F II	23	0	0	- 1	0	- 2	- 3	0	- 2	- 3	- 1	7	4
	35	0	- 2	- 6	1	- 4	- 6	- 1	- 5	- 6	- 2	0	8
	50	- 2	- 14	- 29	- 2	- 15	- 30	- 3	- 17	- 34	- 8	- 24	- 26
	80				- 43	- 78		- 54			- 67		
GEVACOLOR PRINT 1986	23	0	- 2	- 2	0	- 1	- 3	- 1	- 2	- 2	0	- 1	- 4
	35	0	- 3	- 8	5	- 4	- 10	- 1	- 31	- 10	- 4	- 13	- 12
	50	- 6	- 9	- 33	- 4	- 33	- 54	- 9	- 43	- 69	- 15	- 63	- 68
	80				- 80	- 81		- 81					
3 M COLOR POSITIVE HP 895	23	- 1	2	- 2	- 2			0	0	- 2	- 2	0	- 2
	35	- 4	56	- 23	- 3			- 1	- 10	- 21	- 7	- 7	- 25
	50	- 13	- 12	- 72	- 12			- 6	- 20	- 73	5	- 49	- 68
	80				- 84	- 84		- 81			- 74		
3 M COLOR POSITIVE 881	23	2	- 3	- 4	- 3	- 2	- 4	- 1	- 2	- 1	1	- 2	- 3
	35	0	- 11	- 19	- 3	- 12	- 22	- 2	- 9	- 19	0	- 11	- 23
	50	- 7	- 21	- 70	- 10	- 53	- 77	- 8	- 28	- 21	- 8	- 55	- 75
	80				- 86	- 82		- 84			- 76		

* En pourcentage pour une densité moyenne initiale de 1
 Les colorants jaune et magenta ont subi peu de modification, en conséquence les résultats les concernant ne figurent pas dans ce tableau.

TABLEAU N° 1 (suite)

Echantillons	T°C	25 % H.R.			40 % H.R.			65 % H.R.			85 % H.R.		
		6 mois	1 mois	12 mois	6 mois	1 mois	12 mois	6 mois	1 mois	12 mois	6 mois	1 mois	12 mois
CIBACHROME transparent	23	0			2		- 1	1			- 2		
	35	0			- 3		0	1			1		
	50	0	1		0		- 1	0			2		
	80		- 2		- 2			- 41					
FUJICHROME R 100	23	0	- 2		0		- 3	- 1		- 2	- 1		1
	35	- 1	- 8		- 1		- 9	- 8		- 12	- 5		- 2
	50	- 7	- 38		- 3		- 33	- 42		- 42	10		- 59
FUJI SINGLE 8	23	- 1	- 2		- 1		- 2	- 2		0	- 1		5
	35	- 2	- 6		- 1		- 6	- 4		- 11	- 1		- 1
	50	- 2	- 29		11		- 16	- 24		- 38	- 4		- 24
KODACHROME 64	23	- 1	2		- 1		- 1	0		0	- 2		- 3
	35	- 2	2		- 2		26	0		0	- 4		- 6
	50	- 2	0		34		22	0		- 1	- 10		- 14
	80				- 4		85	- 7			- 1		- 14
CIBACHROME PRINT	23	5			0		- 1	- 1			- 1		
	35	3	1		2		0	- 1			- 4		
	50	0	4		0		0	- 1			- 14		
	80		0		- 10			- 17					
CIBACHROME RC PEARL	23	4	- 1		0		1	- 1			1		
	35	5	1		1		0	- 1			1		
	50	4	0		1		0	- 1			- 4		
	80		9		- 8			- 24			- 36		

VARIATION DE LA DENSITE OPTIQUE* EN FONCTION DE LA DUREE D'EXPOSITION A LA LUMIERE NATURELLE

Echantillon	Colorant	Durée de l'exposition (en jours)									
		7	15	21	51	66	77	83	98		
KODACHROME 64	jaune	- 13	- 25	- 30	- 57	- 65	- 69	- 71	- 73		
	magenta	- 13	- 35	- 44	- 70	- 76	- 77	- 77	- 78		
	cyan	- 1	- 1	- 2	- 5	- 6	- 7	- 7	- 8		
CIBACHROME PRINT	jaune	0	2	1	- 1	- 4	- 3	0	- 4		
	magenta	- 1	0	0	- 7	- 10	- 8	- 6	- 10		
	cyan	- 1	- 3	- 4	- 11	- 15	- 12	- 14	- 18		
CIBACHROME RC PEARL	jaune	- 1	1	0	- 2	- 6	- 4	- 2	- 6		
	magenta	- 4	- 2	- 5	- 11	- 13	- 14	- 12	- 15		
	cyan	- 1	- 4	- 4	- 9	- 16	- 16	- 16	- 21		
EKTACHROME 14 RCN	jaune	- 1	- 3	- 5	- 10	- 12	- 14	- 14	- 17		
	magenta	0	- 1	- 3	- 5	- 8	- 8	- 7	- 12		
	cyan	- 1	- 2	- 2	- 2	- 4	- 2	- 2	- 6		
EKTACOLOR 74 RCF	jaune	- 2	- 2	- 2	- 4	- 4	- 4	- 3	- 6		
	magenta	- 5	- 3	- 3	- 5	- 6	- 5	- 5	- 7		
	cyan	- 10	- 7	- 8	- 7	- 9	- 7	- 8	- 9		
PAPIER FUJI COLOR	jaune	- 2	0	- 3	- 8	- 11		- 14	- 25		
	magenta	- 2	- 1	- 2	- 11	- 19		- 29	- 39		
	cyan	- 4	- 3	- 3	- 7	- 10		- 10	- 13		
3 M PAPIER COULEUR	jaune	- 2	- 2	- 2	- 6	- 6	- 8	- 6	- 9		
	magenta	- 3	- 1	- 4	- 5	- 4	- 7	- 4	- 10		
	cyan	- 5	- 4	- 6	- 4	- 4	- 7	- 4	- 16		

* En pourcentage pour une densité moyenne initiale de 1.

T A B L E A U N ° 2 (suite)

VARIATION DE LA DENSITE OPTIQUE* EN FONCTION DE LA DUREE D'EXPOSITION A LA LUMIERE NATURELLE

Echantillon	Colorant	Durée de l'exposition (en jours)									
		7	15	21	51	66	77	83	98		
EASTMAN COLOR 5247	jaune	- 1	- 2	- 2	- 3	- 5	- 4	- 3	- 1		
	magenta	2	2	2	- 1	- 5	- 7	- 8	- 12		
	cyan	- 3	- 4	- 5	- 5	- 5	- 4	- 7	- 9		
FUJI COLOR F 2	jaune	0	- 1	- 2	- 6	- 9	- 12	- 11	- 10		
	magenta	- 2	- 1	- 2	- 4	- 4	- 4	- 5	- 5		
	cyan	- 2	- 1	- 2	1	- 1	- 1	- 3	- 15		
GEVACOLOR PRINT T 986	jaune	- 2	- 5	- 8	- 29	- 46	- 57	- 64	- 71		
	magenta	- 10	- 19	- 29	- 82	- 70	- 75	- 73	- 75		
	cyan	- 2	- 3	- 4	- 5	- 8	- 10	- 11	- 15		
3 M COLOR POSITIVE HP 895	jaune	0	0	- 3	- 10	- 16	- 19	- 22	- 27		
	magenta	- 6	- 12	- 17	- 48	- 69	- 76	- 79	- 80		
	cyan	0	0	- 1	- 4	- 10	- 4	- 10	- 12		
3 M COLOR POSITIVE 881	jaune	- 6	- 9	- 13	- 24	- 31	- 37	- 42	- 49		
	magenta	- 3	- 5	- 7	- 14	- 23	- 29	- 34	- 44		
	cyan	- 3	- 3	- 5	- 8	- 8	- 11	- 12	- 15		
CIBACHROME TRANSPARENT	jaune	- 1	- 1	- 2	- 3	- 3	- 3	- 3	- 3		
	magenta	- 2	- 3	- 4	- 7	- 7	- 8	- 9	- 11		
	cyan	0	0	- 2	- 7	- 11	- 11	- 13	- 17		

* En pourcentage pour une densité moyenne initiale de 1.

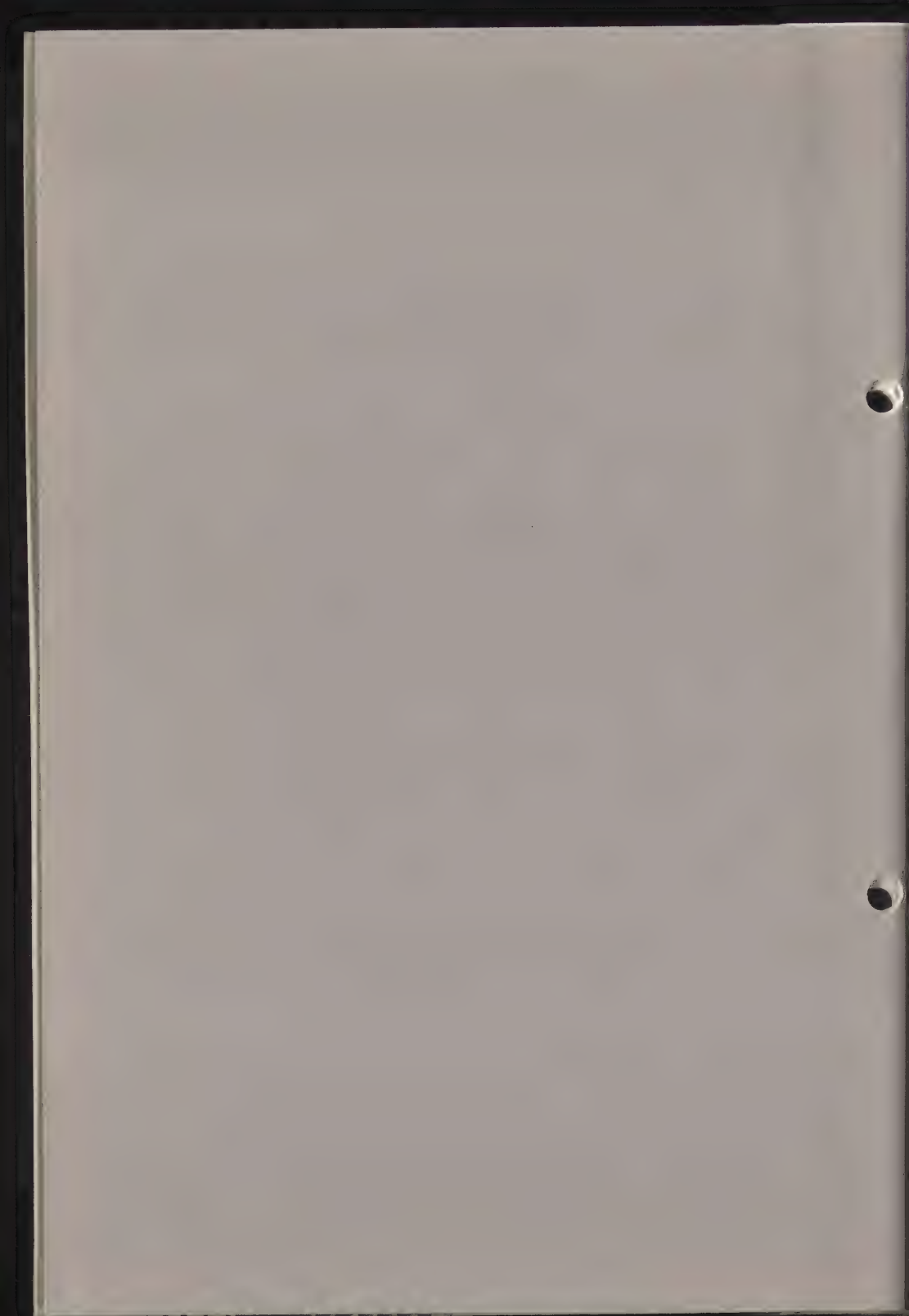
81/14/22

SOME PRACTICAL ASPECTS OF THE STORAGE AND
DISPLAY OF STILL PHOTOGRAPHS

Thomas John Collings

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Graphic and Photographic
Documents



SOME PRACTICAL ASPECTS OF THE STORAGE AND DISPLAY OF STILL
PHOTOGRAPHS

Thomas John Collings

Materials Science Section
Camberwell School of Art and Crafts
Peckham Road
London SE5 8UF
Great Britain

Abstract

The factors influencing the permanence of still photographs are discussed together with their affect on storage and display recommendations. The importance of using the correct quality of materials is stressed bearing in mind the long periods for which the photographs are in contact with them.

Suggestions are put forward for the practical solutions for the storage of glass negatives, whole and broken, paper prints, whether mounted or not, albums, cased photographs and colour photographs and others. Modifications for existing storage boxes to make them suitable for conservation use are discussed.

Some fundamental questions are asked with respect to display of still photographs and suggestions made for improvements to existing mounting and framing methods. A solution for modifying existing frames to meet conservation standards is also given.

"Respectability" is a word which has only in the last decade been applicable in the museum context to photographs as being of real historical importance, either as objects of intrinsic value themselves or as records of particular events. Because of this, large collections have been amassed over the years without proper concern for their conservation. This presents the would-be conservator with a vast backlog of material in urgent need of attention. The situation is further complicated by the very nature of collections, very large numbers of individual and very varying pieces, often where each is of relatively low value but en masse of extreme value. The situation is further exacerbated when recommendations for implementation of conservation procedures sometimes involve real practical problems when attempts are made to put them into practice. The aim of this paper is to provide some solutions which take into consideration these problems.

There are many opinions on what is meant by the permanence of photographs from the 'photographer' who regards permanent as being perhaps ten to fifty years to the 'museum person' who envisages a much longer time span. These differences, which in practice are very real, do present considerable problems when the application of recommendations is under discussion. In this paper the longer time span is regarded as the norm and the recommendations are towards that end.

There are many aspects of photographic conservation which are important but not all are relevant to the vast array of photographic types existing. Two major areas which do are those of storage and display. Whilst it is often glamorous to deal with Daguerreotypes or salted paper prints, the vast majority of collections hold very much larger numbers of gelatine and albumen paper prints and their associated negatives where storage in particular is not very glamorous but nevertheless one of the most important factors involving their permanence. It is important when dealing with specific aspects of conservation to place those aspects in the context of the whole. However, whilst in many areas of conservation this is a relatively easy task, with photographs there are complications, which relate directly to materials present in the photographs themselves. It is naive, and indeed dangerous, when considering factors, to relate them only to the photographic image and to exclude the support materials. If one considers, for example, the range of materials present in one type of photograph, a cased Daguerreotype, one begins to appreciate the order of the complexity (Fig. 1).

MATERIALS ENCOUNTERED WITH A DAGUERRETYPE

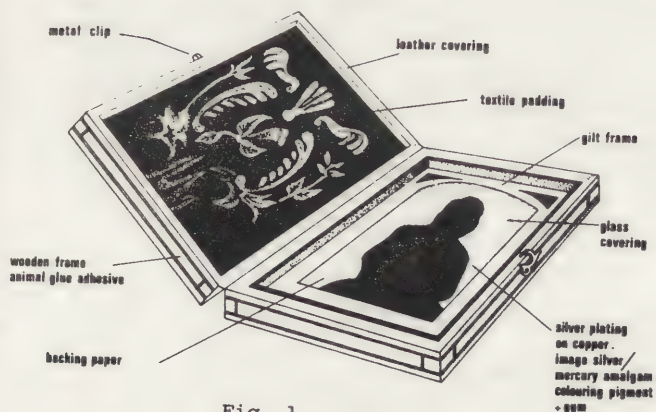


Fig. 1

In general, however, the overall factors which have to be considered may be divided into two general categories:

- (a) internal factors, i.e., inherent properties of the individual materials themselves and those relating to the chemical factors from their manufacture and processing.
- (b) external factors, i.e., temperature, relative humidity, pollutants, light, mould and insect attack, handling.

When considering storage and display, all of these factors need to be taken into consideration, but obviously some are more directly related than others.

Whilst it is not intended in this paper to cover all aspects of storage and display, concentrating particularly on the more practical aspects of systems, a brief coverage of some of these factors is still important.

Temperature and relative humidity are so closely related in influencing deterioration that it is proposed to treat them together. There are numerous publications which give recommendations for storage conditions in particular and the apparent differences which occur are often regarded as confusing. However, if one considers the range of materials which have to be conserved and the varying conditions ideal for each, it is perhaps not surprising that such difference do occur. In every case a compromise has to be made to find the best conditions which will suit the individual complex items themselves, a compromise which should take into account the lower rates of chemical reactions at lower temperatures and the practical problems associated with preconditioning for and retrieval from low temperature storage. Thus it is quite feasible to recommend a storage temperature of below 2°C and 30-40% relative humidity in one case for colour negatives and positives and below 20°C and 15-50% relative humidity in another for silver-gelatine cellulose ester negatives. However, whilst accepting this, there is still further research necessary in some areas to establish the best compromise conditions for particular mixtures of materials.

The silver and colour images themselves exist in a form which is extremely sensitive to pollutants, both gaseous and non-gaseous, indeed there can be few materials or image forms as sensitive. It follows, therefore, that the gaseous pollutants present in the atmosphere which will affect the photographic image are of prime importance. Such pollutants will include sulphur dioxide, hydrogen sulphide, ammonia, ozone and oxides of nitrogen.

Some oxides of nitrogen can, however, be produced from within the photographic collection itself. Nitrate film, whilst being highly inflammable, will be decaying at ambient temperatures with the evolution of these gases, nitrogen dioxide in particular.^{14,15} This gas will cause the deterioration of most organic materials in addition to the silver image itself. The importance cannot be over-emphasised, therefore, of the segregation of all nitrate film from the bulk of any collection. The identification of nitrate film appears in the literature to be simple, but the author has found a number of anomalous examples which, in particular, do not conform to the standard identification tests based on specific gravity using organic solvents.¹⁶ These results are difficult to explain.

Pollutants need not always be in a gaseous form. These may originate from processing or from some older storage materials or mounting systems. The use of ground-wood board for mounting of paper prints has been the norm for many years now. This causes both physical and chemical damage and must be regarded as a major area of concern when one considers the number of mounted prints involved. Storage enclosures, e.g., sleeves, envelopes and boxes, can also cause deterioration by the migration of pollutants from themselves into the photograph. Most of the older, well-established storage systems were introduced before there was any understanding of factors which might cause deterioration. It is not surprising, therefore, to find most unsuitable materials having been used and, in some cases, still being used. During storage, photographs are in intimate contact with other materials for long periods so that purity is of extreme importance. Specifications^{17,18} and evaluation tests¹⁹ for these storage materials are few in the literature but are nevertheless vital.

Handling is a major source of danger which is often overlooked, a danger for most museum objects but photographs in particular. There are more than the usual dangers from physical damage, chemical damage associated with, for example, transference of sulphides from the skin to the silver image also occurs. Protection to permit handling without damage is therefore essential.

The Royal Photographic Society introduced a procedure which insisted those examining prints wore white cotton gloves. This approach, as well as ensuring no skin contact, gives the correct approach to careful handling. It is regrettable, however, that very recently the R.P.S. have ceased this procedure.

Storage - If one now considers possible ways of storing the various types of photographs, bearing in mind the factors mentioned above, certain practical solutions are possible. The following are some examples:

Glass Negatives - As well as being chemically safe, it is essential that the system protects the glass negative from physical damage. It is difficult to justify the use of the 'slide in' type negative bags, which are widely used, when damage by scratching or removal of flaking emulsion is only too possible when glass negatives are slid in and out. Additionally, with those manufactured from paper, the negative has to be removed from its bag for viewing. In 1975, the author designed a simple envelope which wrapped around the negative so that the negative was placed in position with the emulsion against the back of the envelope and the sides and front folded over. Viewing is possible without removal of the negative from the envelope so the chances of scratching and emulsion damage are minimised. The basic shape is as in Fig. 2 and is made from photographic conservation quality

paper. These envelopes are manufactured in the U.K. in standard photographic sizes, but are of a design which can be copied by a conservator, or modified to suit specific needs.

The storage of broken glass negatives presents additional problems not just in safe storage but permitting a retrieval system which, ideally, is identical to that for whole glass negatives. Systems suggesting sticking these to a secondary sheet of glass using pressure sensitive tape, epoxy resin or instant adhesives do not give the necessary protection and require special storage. The following system for mounting the fragments of the broken negative is designed to give the necessary protection as well as permitting it to be integrated into the normal retrieval system. The materials used in this

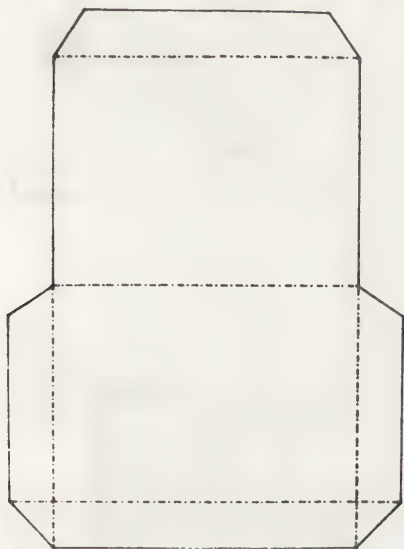


Fig. 2

construction are mounting board, Archive Text paper and acrylic adhesive.

- (i) Two pieces of photographic conservation mounting board the same or slightly larger caliper (thickness) as the glass plate are cut to a suitable photographic size larger than the existing negative. If it is important that the overall negative size not be increased, it will be necessary to make more than one enclosure.
- (ii) The backs of the two boards are coated with acrylic adhesive and left to dry.
- (iii) The broken pieces of glass are suitably positioned on top of one of the boards with about a 10mm gap between adjacent pieces. The outline of each piece is drawn on in pencil (Fig. 3).

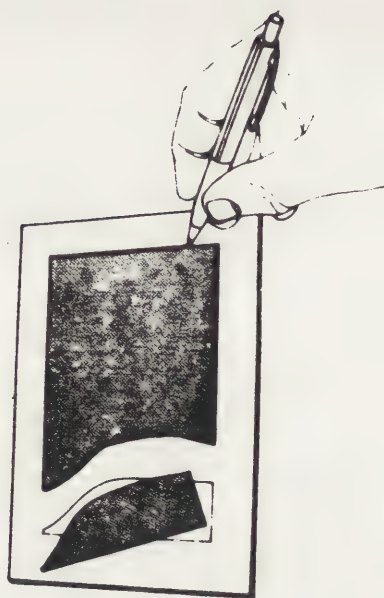


Fig. 3



Fig. 4

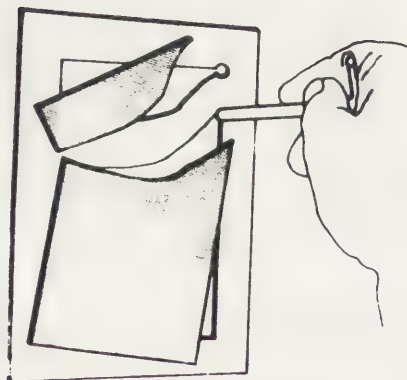


Fig. 5

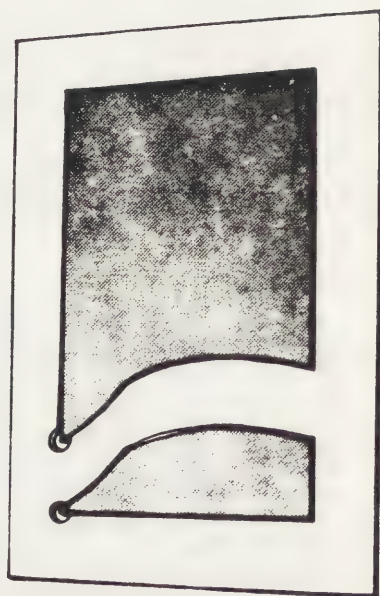


Fig. 6

- (iv) Holes corresponding to the pencilled outlines are cut out with a scalpel so that the pieces fit well, not too lightly or loosely, (Fig. 4), particular care being taken at corners not to make them tight.
- (v) Acute corners on the broken fragments could well become damaged in the mount if the corners are too tight, so to reduce this circular holes are cut into the mount at these points using a laboratory cork borer (Fig.5). The pieces should not fit neatly into the recesses (Fig.6).
- (vi) The recessed board and the other as yet untouched board are positioned on a sheet of the archive text as in Fig. 7

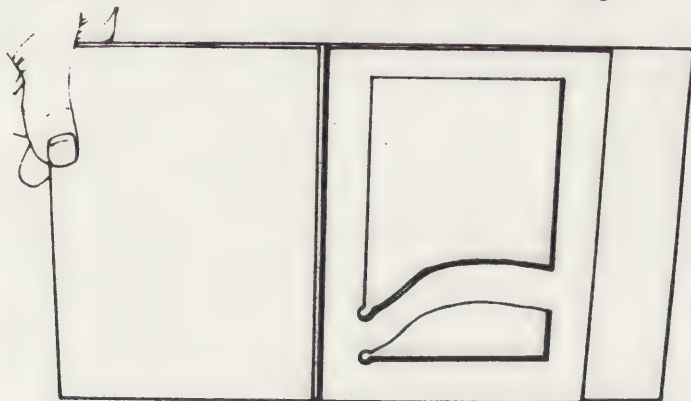


Fig. 7

and the paper heat-laminated onto the back of both boards. The glass negative pieces will then fit into the trays effectively produced by the package, (Fig. 8).

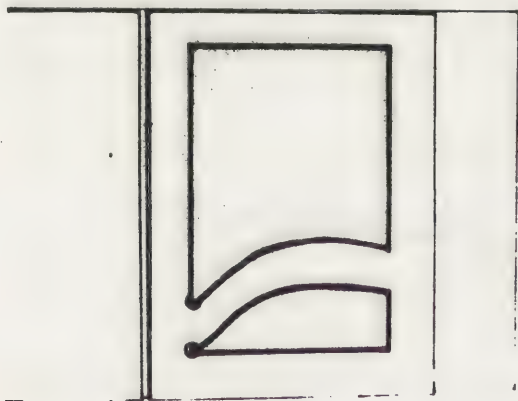


Fig. 8

- (vii) The boards are then folded together and the end flap turned over at the back. If required this enclosure may then be stored in a paper envelope as described earlier.

It is felt that this system has a number of advantages over others in that the negative pieces are well protected, cannot rub against one another and will permit easy viewing and assembly if required. Additionally, because the overall size conforms to the photographic sizes, it will fit into the normal storage and retrieval system for glass negatives.

Glass Negative Storage Boxes - There are various designs available but users have found two main problems in relation to their use. Firstly, because of the weight of the negatives, the boxes are not substantial enough to give the necessary support and, secondly, which is related to the first, there appears to be no simple method of using spacers between the negatives when required. However, the latter is possible by interleaving with sheets of photographic conservation quality board and the former by choice of a suitable box. In 1975 the author designed a box for glass negatives which is now much used in the U.K.¹⁹ The board is not conservation quality but has a protective polythene laminate on the inside which tests, including the silver tarnish test,²⁰ have shown to be satisfactory. As a precaution against possible condensation problems caused by temperature fluctuations, which might occur in unsuitable storage conditions, filtered air circulation holes are built into the sides of the box. Whilst it is accepted that chemically it might be better to have a box constructed of the "correct" quality board, this board is still safe, strong and can be produced at approximately one half the price of other boxes. The box was designed and manufactured specifically for those museums on a limited budget in the U.K. but has found use beyond this.

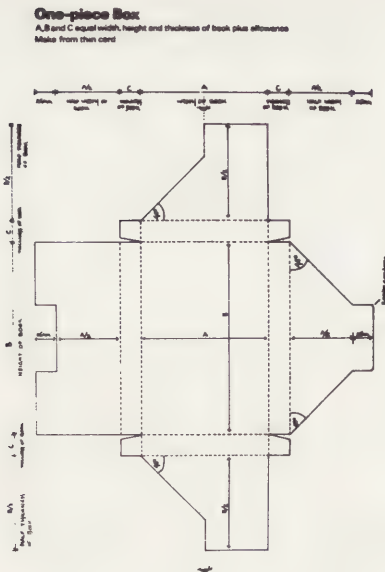
Paper Prints - The problems associated with paper print storage relate to two main types, those mounted and those unmounted. Those mounted often present the conservator with the problem of the poor quality of the mounting board, and the decision to remove the print from its mount or not. This argument aside, there is still the problem of storage. The various systems which are used include flat storage in piles in 'solander' type boxes which present problems on retrieval of causing physical damage whether the prints are interleaved or not. Alternatively the prints may be stacked vertically on open shelves or in filing cabinets, again often with little protection. Whilst it is perfectly possible to store prints in 'solander' type boxes or in cabinets, it is essential that protection be given to ensure that the necessary support is provided and that retrieval can be undertaken safely. There are two basic ways in which this can be achieved, both using plastic enclosures. Whether the print is mounted or otherwise it is advisable to support it using photographic conservation quality board,²¹ to give added protection from bending if unmounted or fracture if mounted particularly if on an embrittled board. The support board should be just larger than the photograph which it is protecting. The print and support board is then wrapped in a polyester film,²² the same width as the support board, double sided pressure sensitive adhesive tape²³ being used to form it into a sleeve on the back of the support board. The sleeve provides good

protection and visibility whilst the addition of cellulose material in the form of the support board will help stabilise the relative humidity inside of the sleeve against possible external changes. The second method involves using a self-sealing polythene bag instead of the sleeve. This method is usually cheaper, as safe chemically, and will give more protection from gaseous pollutants than the sleeve. However, the aesthetic nature of the material is found by some to be unacceptable and the clarity is inferior, additionally some consideration must be given to conditioning the print and board to its storage temperature and relative humidity before sealing.

A problem which is often said to occur when some plastics are in intimate contact with photographic emulsions is that of glazing or ferrotyping. Whilst the author has no evidence of this occurring with paper prints, if it is felt that it might be a problem then it will be necessary either to mount the print in a window mount, described later, or to wrap the print in a suitable tissue before placing it in the plastic enclosure. Of course the latter will negate the advantage of being able to view the print without removal.

Cased Photographs and Others - The use of sealable polythene enclosures gives considerable protection with virtually any type of cased photograph, but it is essential with many cases, e.g., Union cases to wrap the case in a tissue to provide additional protection. The protected cases can then be stored in suitable storage boxes with the knowledge that the polythene will provide additional chemical protection. Again, however, conditioning before sealing may be necessary. Tin types (ferrotypes), photographs in wood, metal, ceramic, lantern slides may each be protected by using the tissue and polythene enclosures system but the inclusion of a suitable board support is recommended. This is a system which is very versatile, safe and not expensive.

Albums - Many of the Victorian albums which are held in collections today are in a damaged condition. Many are on board which has a high proportion of ground/mechanical wood which has deteriorated and embrittled. Conservation of the complete object, album and photographs, is a major ethical as well as conservation problem. However, leaving them on open shelves gives little protection. One method which is often used is to wrap the albums in a suitable paper with a strap around it supporting the spine, or alternatively, custom built enclosures are possible. A design of one is given in Fig. 9 by Mr Alan Howell, a conservator in the U.K. In each case the protected album should be stored in a suitable box.



Alan Howarth
May 1979

Fig. 9

Colour Photographs

Problems associated with the permanence of coloured photographs are many and bad storage systems can only exacerbate the situation. Coloured prints can be stored as has been described for other paper prints but transparencies and negatives present additional problems. Whilst it is accepted that card mounts for transparencies are unacceptable the ideal mount of aluminium and glass alone does not appear to be available yet. For negatives and transparencies which are not going to be projected, storage in polyester sleeves gives probably the best protection at this moment in time, but they are by no means a fully satisfactory solution.

Storage Boxes

Many, perhaps most, collections are housed in boxes which are not of the correct quality.

Adhesives, the board itself and

covering materials are often unsuitable, but to recommend complete replacement would result in considerable cost. However, there are methods whereby the contents of the box can be protected from any dangers which might emanate from the box itself. This is achieved with the use of an impervious liner, of which at least two types exist. There is a material marketed for laboratory use called 'Benchkote' which is a blotting paper polythene laminated on one side. The paper side is compatible with most adhesives and can be attached as a liner to the inside of the box, the polythene layer innermost. Alternatively, aluminium foil can be used. If the foil is pre-coated with an acrylic adhesive, it can be heat sealed into place inside the box. Both of these liners will protect the contents from any migration of pollutants from the box. However, there is a possibility, under incorrect storage conditions, and in particular temperature changes, of producing, in the extreme, conditions below dewpoint. If this is a possibility then some filtered air circulation is necessary.

Building filtered air vents into a box can be achieved by one of two methods. With board boxes it is possible to cut, or bore, a hole through the box wall and liner and to cover the outside of the hole with a thin cartridge paper, ensuring that there is no adhesive on the paper where it covers the hole, to act as a filter. It is important that the hole(s) not be too large, perhaps 10mm diameter

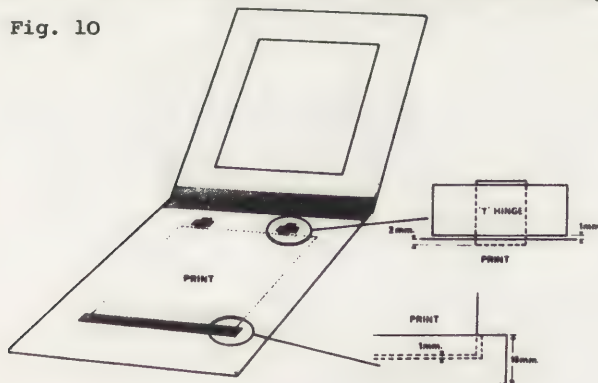
maximum, as there might otherwise be a problem of breaking the filter seal with ones fingertips when picking up the box. If the box is of a wooden construction, e.g., a 'solander' box, a technique suggested by Mr Sandy Cockerell, the bookbinder, is worth consideration. A hole is drilled through the box and liner the same diameter as a standard cigarette filter and after drilling the hole is plugged with such a filter. The system is easy to establish and the filters are easy to replace being obtainable from any tobacconist.

Display - When display is considered, there is one fundamental question which first must be answered. This relates to the need or otherwise of displaying the original. There is an increasing trend, especially with colour and early silver photographs, to display copies only. Since moving the objects from conditions of storage to ones of display will almost inevitably involve some form of climatic change, it follows that display of originals should be minimised to minimise the problems associated with such changes.

Additionally, some thought should be given to the maximum length of time a photograph ought to be displayed. Although the established light quality and quantity levels recommended for works of art on paper are regarded as suitable for most non-colour materials, no time limit is given.⁴⁴ There is a school of thought originating from the Tate Gallery that the total light energy falling on the display object is more relevant. To this end a 'total dose' light meter⁴⁵ reading in lux. hours has been developed to monitor this parameter. To date the research which has been carried out with this instrument has been orientated towards oil paintings but, nevertheless, it would be of value to relate this to the present recommendations for photographic materials.

Mounting - Whilst mounting of prints is a well-established technique, there are still a few problems existing. These include, difficulty in obtaining mount hinge material of the correct quality, problems with adhesives swelling the emulsion locally and troubles associated with thin albumen prints coiling themselves up. Fig.10

Fig. 10



gives an arrangement which goes some way towards providing solutions to these problems.

The mount itself is of a suitable conservation quality and the hinges between the matt and the mount backing are made using Archive Text paper pre-coated with an acrylic adhesive and heat-set in position. The type of hinges to hold the print in place are an improvement on the 'stamp hinge' or straight type as the cross piece of the hinge gives strength and stability so that side-ways slack of the print is reduced to a minimum.

The hinges are made from Archive Text¹⁸ rather than Japanese tissue, which has been recommended often. The reason for this is that the author has found, over the years, a regression in the quality of certain Japanese tissues originating often from poor stock preparation of the fibres. This has resulted in bark elements occurring in the paper and hence presenting problems relating to their high lignin content. It is felt safer, therefore, to recommend a material whose properties are more constant.

The adhesive for the hinges is acrylic³¹, the hinges being pre-coated. The vertical hinge is first heat-set onto the top edge of the underside of the print using a tacking iron. It is not necessary to extend the hinge more than 2mm on to most joints as the adhesive has far greater strength in this form, than most water-based adhesives. The print is then positioned on the back board and the cross pieces of the hinge heat-set in position. This procedure can be carried out very quickly and safely with no swelling problems of the emulsion occurring. Removal is simple also. As only 2mm of the hinge extends under the print it is possible for a conservator to remove it dry with a scalpel. Alternatively, moistening the hinge with a little acetone will dissolve the adhesive and hence effect the necessary hinge removal.

The curling of prints when mounted may be at least reduced by inserting the bottom of the print into a thin pocket made from Archive Text³ which has been pre-coated with the acrylic adhesive and then heat-set in position. There is no form of adhesive holding the bottom of the print in position so that some movement is still possible.

The mounting of prints is expensive and care must be taken to ensure that the mount, as well as the photograph, is well protected. Encasing the mount in a polyester sleeve³², as described for paper prints, will ensure the necessary protection.

Framing

Fig. 11 is an arrangement designed to give the maximum amount of physical and chemical protection to a print which has been framed

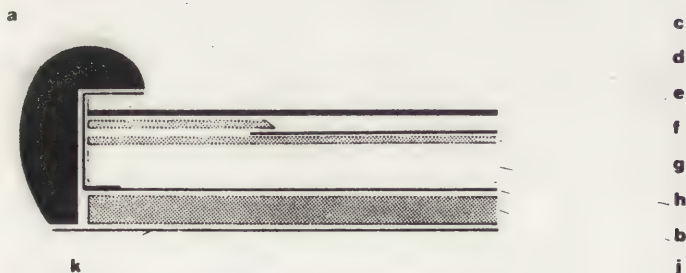


Fig. 11



for display. The lettering on the arrangement refers to the following: (a) frame moulding; (b) aluminium foil; (c) glass; (d) U.V. polycarbonate; (e) bevelled matt; (f) print; (g) mount backing; (h) filter paper on board bed; (j) backing board; (k) paper, edge dust seal; (l) depth extension.

A problem which has been found when exhibiting prints is that it has been recommended that contemporary wooden frames should not be used, only frames made from aluminium. There has been a quest, therefore, to find a solution which would permit the safe use of frames which artistically would suit the images better. One suggested solution is to line the inside edges of the frame with aluminium foil, which may be pre-coated with an acrylic and heat-set in position if required, to act as an impervious layer to protect the photograph from any migrating pollutants. In this way restrictions on the use of certain frames may be lifted. To protect the photograph from ultra-violet light, usually a U.V. acrylic sheet is suggested. (The author acknowledges, of course, that during exhibition no U.V. light should be present anyway.) However, polycarbonate is available in a thinner sheet (1.5mm) than the acrylics, is colourless, has excellent transparency and is chemically safe in this context. It has additional advantage, that it is very tough and has a high impact resistance. It is used to make motor cycle visors, for example, so that considerable physical protection is given, especially if the frame receives accidental damage and the glass is broken.

The function of the bed of cellulose material behind the print mount

is to provide a buffer to the contents of the frame from changes in atmospheric conditions externally. The property of cellulose to absorb from or emit to air water vapour naturally enables it to provide a much more stable environment.²⁴

The aluminium foil extends across the back of this cellulose bed to act as a seal; standard or even the original backing boards can then be used.

However, not all frames will be capable of accepting all of the layers suggested above and some modification of the frames will be necessary. The basic problem is that the depth is inadequate. This may be increased by screwing square cross section lengths of planed wood to the back of the frame, '1' in the insert on Fig.11, of such a thickness that the depth is increased to about 10-15mm. Because this additional framing will be lined with the aluminium foil, the type of wood used is not particularly important. This simple addition will make it possible to use almost any frame without altering in any way its external appearance when hung.

Conclusions - Conservation involves many factors, personal and technical, and whatever is advised, by the very nature of people and materials, will not be wholly acceptable. The author, in this paper, has tried to present solutions to a number of conservation problems, the success of which will depend on their simplicity in practice. Mr David Baynes-Cope of the British Museum has a saying "conservation is a balance of risks". It is to be hoped that the information given will tip the balance in our favour.

References

1. Ostroff E., "Preservation of photographs", The Photographic Journal, Oct.1967, pp 309-314.
2. Harker M., "The Gelatino-Halide emulsion printing processes, R.P.S. Conference, 1974, The Recognition of early photographic processes, their care and conservation.
3. Coe B., "The early paper processes", R.P.S. Conference, 1974, The Recognition of early photographic processes, their care and conservation.
4. B.S.1153: 1975 "Recommendations for the processing and storage of silver-gelatine-type microfilm".
5. B.S.5454:1977 "The storage and exhibition of archival documents"
6. Collings T.J., Young F.J., "The care of photographic collections" Area Museums Service for S.E. England, 1977.
7. I.S.O.5466 Photography - Practice for the storage of processed safety photographic film, 1980
8. I.S.O.6051:Photography-Silver image photographic paper prints for record purposes, 1980.
9. Adelstein P., Graham C.L., West L.E., "Preservation of motion picture color films having permanent value", Journal of the S.M.P.T.E., Vol.79, Nov.1970, pp 1011-1018.
10. Giles C.H., Haslam R., "The keeping properties of some colour photographs", Journal of Phot.Soc., Vol.22, 1974, pp 93-96.
11. Collings T.J., Young F.J., "The care of colour photographs", Area Museums Service for S.E. England, 1978.

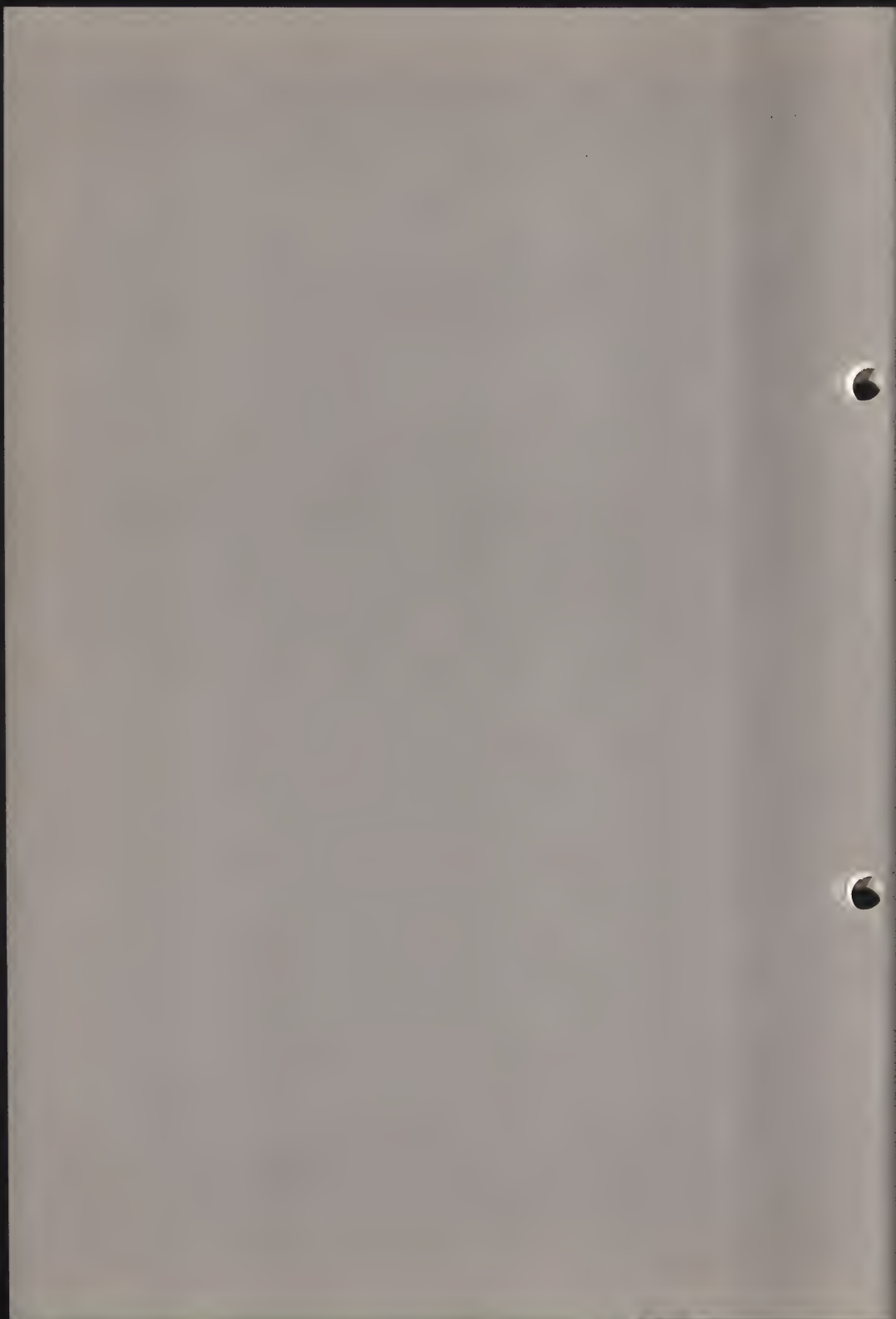
12. Calhoun J.M., "Storage of nitrate amateur still-camera film negatives", Journal of the Bot.Phot.Assoc., Vol.21, No.3,1953, pp 1-13.
13. Cummings J.W., Hatton A.C., Silfin H., "Spontaneous ignition of decomposing cellulose nitrate film", Journal of the S.M.P.T.E., Vol.54, March 1950, pp 268-274.
14. Rempel S., "The care of black and white photographic collections - identification of processes", C.C.I.Tech.Bull.No.6.
15. Collings T.J., Young F.J., "Improvements in some tests and techniques in photographic conservatio", Studies in Conservation, 21,1976, pp 79-84.
16. American National Standard, "Requirements for photographic filing. Enclosures for storing processed photographic films, plates and papers".
17. Baynes-Cope A.D., Collings T.J., "Some specifications for materials and techniques used in conservation of archives, Journal of the Soc.Arch., Val.6, No.6, Oct. 1980, pp 384-386.
18. "Archive Text", 85g/m² P.F.Bingham & Co.Ltd., Leatherhead, Surrey, England.
19. G. Ryder & Co.Ltd., Denbigh Road, Bletchley, Milton Keynes, England
20. "Antique Mounting Board", The Drayton Printing Works, Sonta Park, Fulham, London, England.
21. "Primal AC 61", Rohn and Haas (UK) Ltd., Lennig House, 2 Masen Avenue, Croydon, Surrey
22. To meet U.S.Government specifications L-P-00670 (B2) "Protector, Document" and L-P-377B "Plastic Sheet and Strip, Polyester".
23. 3M Scotch Brand Double Coated Tape No. 415.
24. Thomson G., "The Museum Environment" I.I.C.Butterworths, 1978.
25. "Lens Tissue", J.Barcham Green Ltd., Bayle Mill, Maidstone, Kent. England.
26. Secol Ltd., Kelvin Place, Thetford, Norfolk, England.
27. "Benchkote", Whatman Labsales Ltd., Springfield Mill, Maidstone, Kent, England.
28. Integrating Light Meter Type 790. Littlemore Scientific Engineering Company, Railway Lane, Littlemore, Oxford, England.
29. "Lexan 9034-112", Visigar Laboratories Ltd., 1 Pegasus Road, Croydon Airport, England.



MURAL PAINTINGS AND MOSAICS

Coordinator : P. Mora (Italy)

Assistant coordinator: L. Sbordonì Mora (Italy)



GROUPE DE TRAVAIL PEINTURES MURALES ET MOSAIQUES

Activités du groupe, 1980-1981

Coordinateur: Paolo Mora

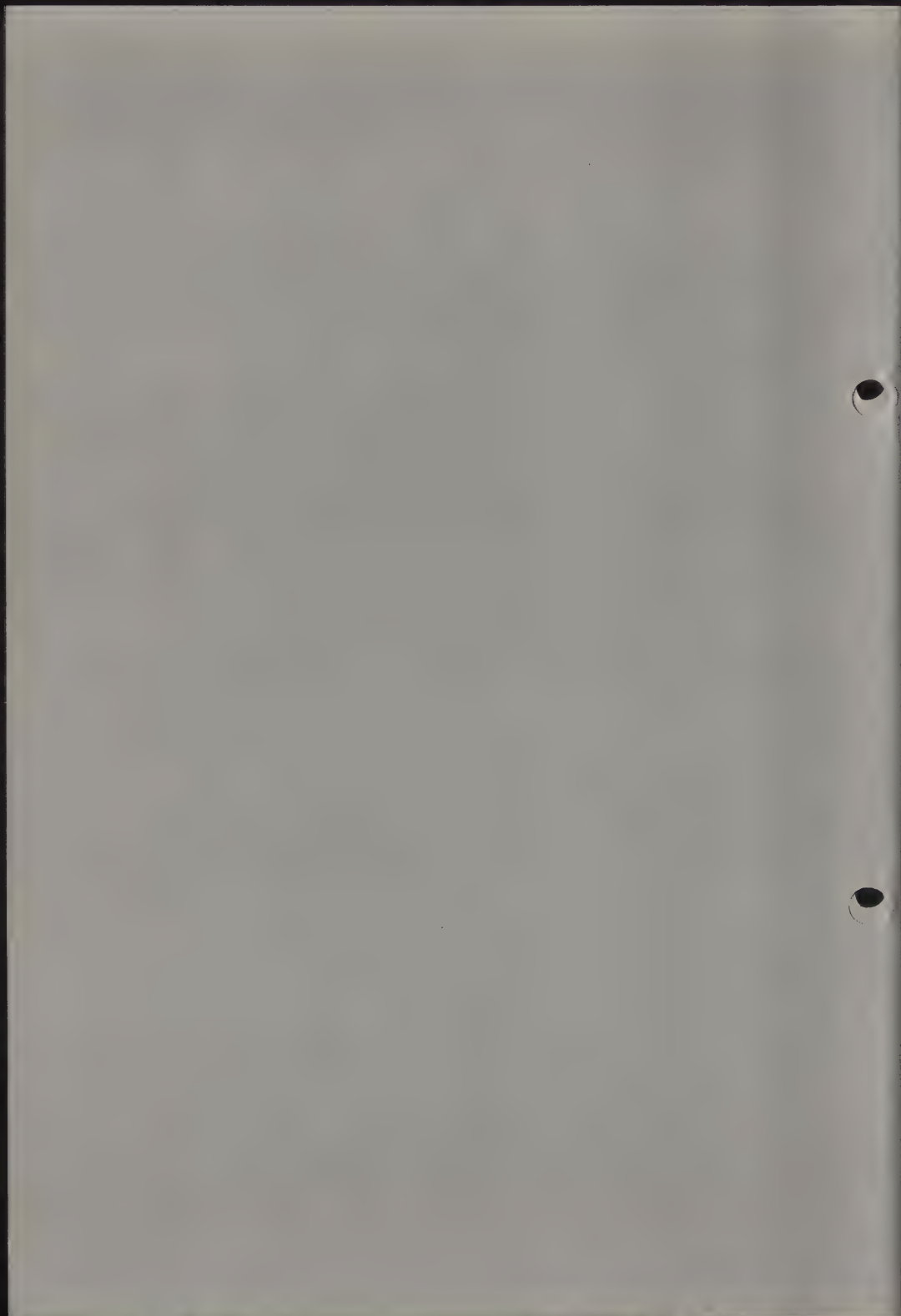
Istituto Centrale del Restauro
9 Piazza S. Francesco di Paola
Roma 00184
Italie

Le groupe de travail n'a pas eu la possibilité de se réunir en vue de la Réunion Triennale de Ottawa, mais ses membres ont produit un certain nombre de rapports très intéressants desquels la liste est ci jointe.

D'autres rapports sont en préparation mais à cause des dates ne pourront pas être présentés cette fois.

Pour ce qui regarde notre travail, nous sommes en train de revoir la traduction en Anglais et en Italien du livre "La conservation des peintures murales" qui est pour tout les deux assez avancée.

Avec l'ICCROM et le Comité pour la Mosaïque on a déjà publié "Mosaïque N.1" et dans un court delai sortira "Mosaïque N.2".

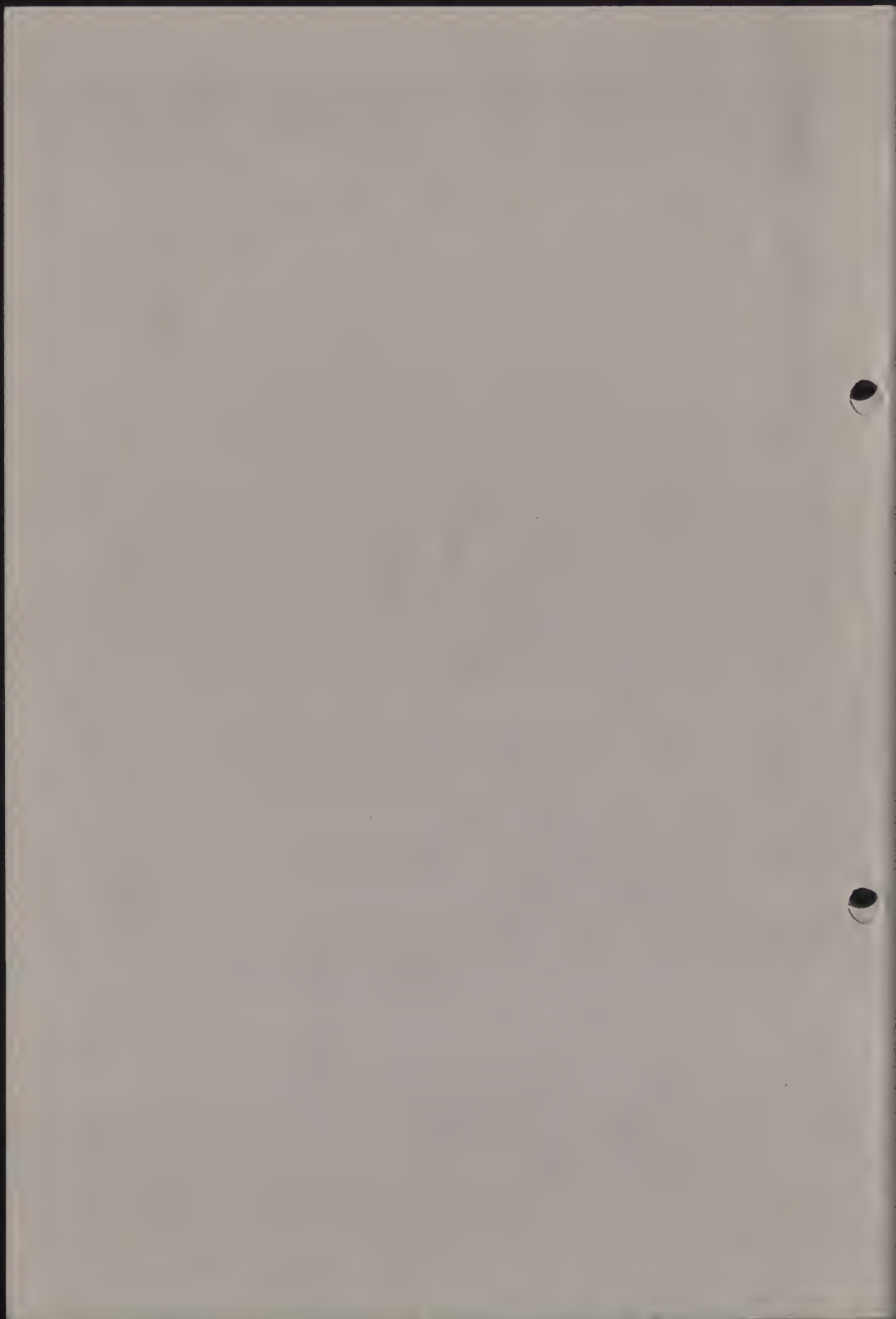


THE RECONVERSION OF OXIDIZED WHITE LEAD IN
MURAL PAINTINGS: A CONTROL AFTER A FIVE
YEAR PERIOD

M. Matteini and A. Moles

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Mural Paintings and Mosaics



THE RECONVERSION OF OXIDIZED WHITE LEAD IN MURAL PAINTINGS:
A CONTROL AFTER A FIVE YEAR PERIOD

M. Matteini and A. Moles

Opificio delle Pietre Dure e Laboratori di Restauro
Florence
Italy

Abstract

In many mural paintings where White Lead was used, such a transformation in a brown product occurred, to modify greatly the chromatic value of the painting.

In 1975 M. Matteini ascertained the nature of the brown derived from the transformation of Biacca and determined a methodology to reconvert it into White Lead. Tests were carried out and gave positive and satisfactory results.

After five years, an accurate control of the areas treated took place and no type of drawback was found. The treatment was therefore given to the whole of the fresco and it is believed that such a methodology can be applied safely on other mural paintings where the same phenomenon of oxidation is present.

On ancient mural paintings where the artist has used White Lead as a white pigment, one can usually observe ugly transformations of the pigment into products of an intense brown colour. The effect is often such as to upset totally the light and shade values of the painting, to such a point as to seem the negative of itself.

As is known, the white pigments which were used in ancient mural painting are, above all, those made up of Calcium Carbonate used by the artist as such or as a result of the carbonating reactions of Calcium hydroxide with atmospheric Carbon dioxide.

The artists normally avoided the use of White Lead on the wall, even though it was precisely this white pigment which was extensively used in all other kinds of painting.

Although the reasons for such mistrust are not made clear in the few quotations to be found in ancient literature (1), one must believe that some obvious, undesirable transformation which the White Lead undergoes if applied to the wall, was a phenomenon amply acquired by the patrimony of ancient experience.

In '76 Matteini, (2), continuing previous studies and analytical controls which had already begun on specimens drawn from the Cimabue frescoes in the Assisi Cathedral, ascertained definitely the nature of the brown product from the transformation of Biacca (White Lead).

A series of X-ray diffractometric analyses of the blackened whites which were also found in the A. Baldovinetti frescoes in S. Miniato (Florence), made it possible to identify the brown compound as Lead dioxide PbO_2 (Plattnerite).

The frescoed lunettes by Baldovinetti in the vault of the "Cardinal of Portugal's Chapel" in S. Miniato, showed such an extensive phenomenon of "blackening" to inspire a group of "fresco-restorers" in 1930 to completely repaint the blackened areas with a white overpainting.

In '75, owing to a new intervention of restoring these same frescoes, the restorer G. Rosi, during the elimination of the old repainting in 1930, revealed the underlying extensive brown areas.

The analytical research carried out on that occasion showed that the white used by Baldovinetti for the execution of the paintings was White Lead and that the dark brown compound, identified as PbO_2 , filled in cross-sections the same level of white pigment (that is the pictorial layer) and therefore acted as its own product of transformation.

It was possible to observe sections of fragments in which one could see, simultaneously, part of the pictorial film still in its original white state and part already transformed into brown.

In some cases the beginning of the transformation came about near the external side of the pictorial layer, in others, on the contrary, on the inner part, in contact with the mortar beneath. (fig.1).

This fact lead to believe that the transformation did not have a preferential spatial orientation, for example externally (due to atmosphere, conservative treatments etc.) or internally (due to substances present or affluent in the mortar beneath).

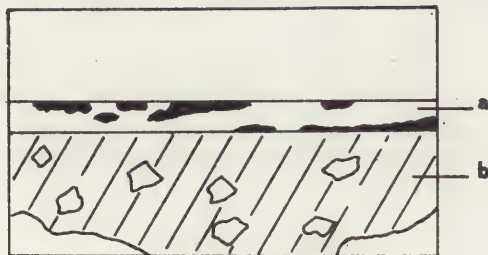


fig.1 schematic drawing of a cross-section of a fragment where White Lead oxidation product (PbO_2) is observable (black) in the paint layer (white - White Lead) a: paint layer, b: mortar.

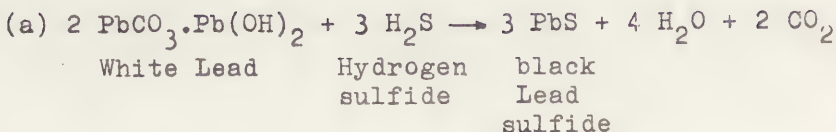
The artist, in many cases, had mixed other pigments with the white pigment, for example Azurite for creating skies or Carbon Black for certain shadings. The fragment sections showed clearly under the microscope that such pigments had not transformed into the mass of the darkened white pigment, even if under the visual observation of the paintings, they were completely masked by the brown colour.

Because of these ascertainments, we realised then how important it would be to recuperate the significant values of the work of art, if it was possible to regress the transformation, reconvertng the blackened White Lead to its original state.

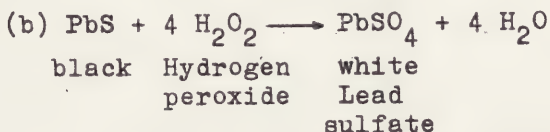
The first and most important research carried out was, nevertheless, that of studying and clarifying the transformation that had come about and possibly to specify the causes.

Having verified the reagents (basic Lead Carbonate) and the products (Lead dioxide), it was possible first of all to distinguish clearly such a transformation of the White Lead from another already known of the same pigment which converts it into grey-black Lead sulphide and which almost only takes place on paper, where the White Lead is dispersed in weak watery temperas.

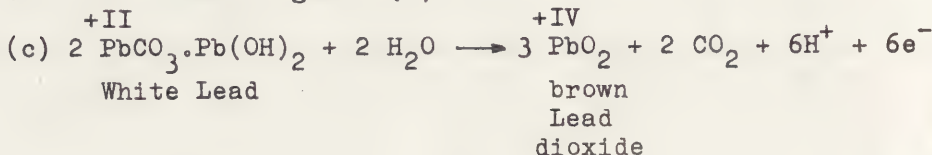
The latter is a double exchange reaction by interaction of the pigment with an acidic gas (H_2S) of the atmosphere (a):



A process of "bleaching" is also known and has been experimented. It is applied in restoration works to eliminate the grey compound which is formed. Hydrogen peroxide is used, taking advantage of the classical oxidative effect of this compound (b):



The transformation which takes place on the frescoes consists instead in a real oxidation of the Lead from + II to + IV oxidation grade (c):



Such a reaction (c) consists, obviously, only in a semi-reaction; the oxidative partner which completes the redox transformation does not in fact appear. Just the research on this oxidising agent needed long and involved studies.

Numerous laboratory tests were simulated on oxidation of Biacca, varying the probable reactive agents, the possible catalysts (substrata, binders, pictorial techniques) and the conditions of reactions (humidity, pH, light etc.). However, under no circumstances, starting from White Lead made to react with non improbable oxidising reagents, PbO_2 or other (+IV) Lead compounds were ever obtained.

Only two transformations were observed and it was established that both took place in an alkaline solution. In one case it consists above all, in a physical phenomenon: in the fresco application of White Lead, the pigment is fixed by the mineral binder, (Calcium hydroxide which carbonates in the air)ⁱⁿ a non homogeneous way with the formation of islands whose geometry reminds those of brown

dioxide which are to be seen on the frescoes.

No Pb (+IV) compound is, however, present in such "islands". The second phenomenon, instead, consists of a precise chemical transformation of White Lead (basic Lead carbonate) into orange Lead mono-oxide when the pigment is left for some time in contact with a solution of Calcium hydroxide.

In the graphic sense of the reaction (c) one can ascertain a development of acidity among the products which suggests an easier reaction in an alkaline ambient.

This is proved in the values of redox potentials of the reaction which appear very high in acidic solution (about +1,8V (Pt) in H_2SO_4 4.82 N) to fall drastically in alkaline solution. (ex. 4 + 2 V (Pt) in KOH 8,4 N). (3;4). In conclusion, if it was not possible to find the causes and the mechanisms which lead to the oxidation of White Lead in mural paintings, we believed, however, to be able to detect as more favourable conditions to the process, the presence of alkalinity especially due to Calcium hydroxide.

Having established the nature of the brown product and consequently that it necessarily comes from a reaction of oxidization the possibility was considered to conduct an opposite process, that is to say of reducing Lead dioxide in safe conditions for the painting.

Maintaining precise and rigorous conditions of selection, a large number of possible reducing agents were discarded, in as much as were thought unsuitable. A restricted number of substances however were individualized to be able to carry out the process.

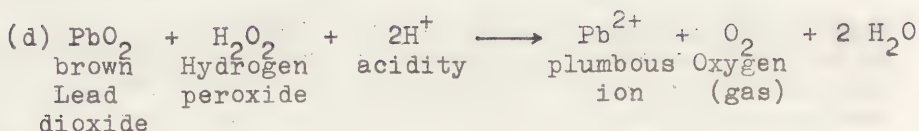
Two of these (Hydroxylamine and Hydrazine) can reduce the Lead dioxide; they are nevertheless strongly reactive substances, capable, therefore, to provoke transformations also in other pigments (i.e., azurite etc.) eventually coexisting with Lead dioxide.

Moreover, the experiments did not provide altogether acceptable results aesthetically speaking.

A third substance, Hydrogen peroxide, revealed instead a very satisfying behaviour under many aspects. The only limitation came from the fact that this compound can only react in a solution at least slightly acidic.

Hydrogen peroxide works, in this case, very differently from the previously mentioned one (reaction b) to bleach the Lead sulphide.

In this case it reacts, in fact, not as an oxidising agent but as a reducing one as opposed to a stronger oxidising substance: Lead dioxide (reaction d):



As one can see, neither the reagents nor the products, all being volatile substances, can pollute the mural painting.

The restrictive condition of the acidity was theoretically studied and experimentally tested in order to define the type of acid to be used, the minimum effective concentration and the possible effects of damage.

After a series of considerations, acetic acid was chosen as the best acidic component.

When using it one can be sure of the real reconversion of the oxidized biacca.

Some natural processes, in fact, convert gradually the Lead acetate which initially forms into basic Lead acetate (hydrolysis) and then into basic Lead carbonate (carbonation), or that is to say, into White Lead which consists, in a basic carbonate.

It was also possible to limit the concentration of the acid used in situ, within values of only 1%. Theoretic calculations finally allowed to ascertain that at such values of concentration the formation of by-products of reaction (with possible damage to the plaster) has to be considered quantitatively negligible being no more than impurities.

In 1976, concluding all the laboratory tests, we then proceeded with the direct application of compresses on the frescoes using absorbent materials impregnated in a water solution of the following composition:

Hydrogen peroxide	.6 ÷ 1%
acetic Acid	1%

The applications were limited however to small restricted areas representative of the frescoes.

In fact, the causes of the brown stains did not emerge clearly in the research which was carried out and it could come about that the pigment, even if reconverted into its original white state, would again oxidize into brown Lead dioxide, after a short period of time.

In this case the intervention would have obviously been useless.

Through compresses kept in contact with the surface of the painting for about fifteen minutes, we obtained completely satisfying results, not only technically but also, and above all, aesthetically speaking.

In fact the oxidative process or, that is to say, the formation of the brown, affected the pictorial film in a major or minor way, according to the areas. Consequently, the reconversion is not homogeneous. This enables one to establish the best moment to stop the process.

In the applications we carried out, we never reached, intentionally, a total reconversion. According to our conservation principles it is right that a trace of such a process remains, whatever the origin, which, historically speaking, has by now affected the fresco. For obvious reasons, this is never the only process of degradation suffered by the work of art. While in other transformations it is never possible to return entirely to the original state, it would be wrong to do it only for this process.

The chromatic values of the whites were recuperated brilliantly in the tests carried out, in the blues of the skies, in the shaded blacks of carbon, etc.

The preliminary results of the tests which took place according to the methodology introduced by M. Matteini were communicated in Florence at the Restoration Congress in 1976. (2).

After five years, a careful visual and analytical control of the results obtained, took place.

Optically one could not establish any change in the chromatic situation which had been reached five years before. The confirmation comes from a precise and careful comparison of the colour photographic documentation carried out at the end of the preliminary tests with updated visual observations in the same points. We also proved that not even in the untreated areas was there found any extension of the transformation into dioxide.

In fact all the outlines of the brown stains, whether of large or microscopic dimensions, appear unchanged. Consequently, at least limitately speaking, for the short period involved (five years), the evolution of the phenomenon of White Lead oxidation is to be considered in a static phase.

In order to control the state of conservation of the treated areas and of possible eventual drawbacks which could have come about, we proceeded to examine the surface and to make chemical analyses both of the pictorial layer and the mortar beneath.

No formation of saline surface efflorescences were observed in the treated areas.

The pictorial surface appears in the same conditions in which it was left immediately after the treatment and not dissimilar in aspect from the untreated areas nearby, even after examining it under tangential light. Neither were phenomena of decohesion nor of lifting of the pictorial film observed.

On the other hand, results of the chemical analyses carried out on specimens drawn from the pictorial film and from the mortar beneath, showed no presence of soluble salts in a greater quantity or different in nature from those coming from untreated areas.

The controls were carried out using microanalytical method tests and by I.R. spectrometry. Characteristic absorption bands of Calcium acetate and of other acetates were especially controlled in the I.R. spectrograms. It was found that such compounds are present in trace quantities as the theoretic estimates forecasted.

Pleased with such positive results which confirm the total lack of possible drawbacks, it was decided to extend the application of the method to all the areas where the transformation of the Lead White had taken place more intensely and where the chromatic context and the aesthetic reading clash more strongly.

Operations in this sense have already begun and the results which have so far been obtained confirm the total validity of the method.

References

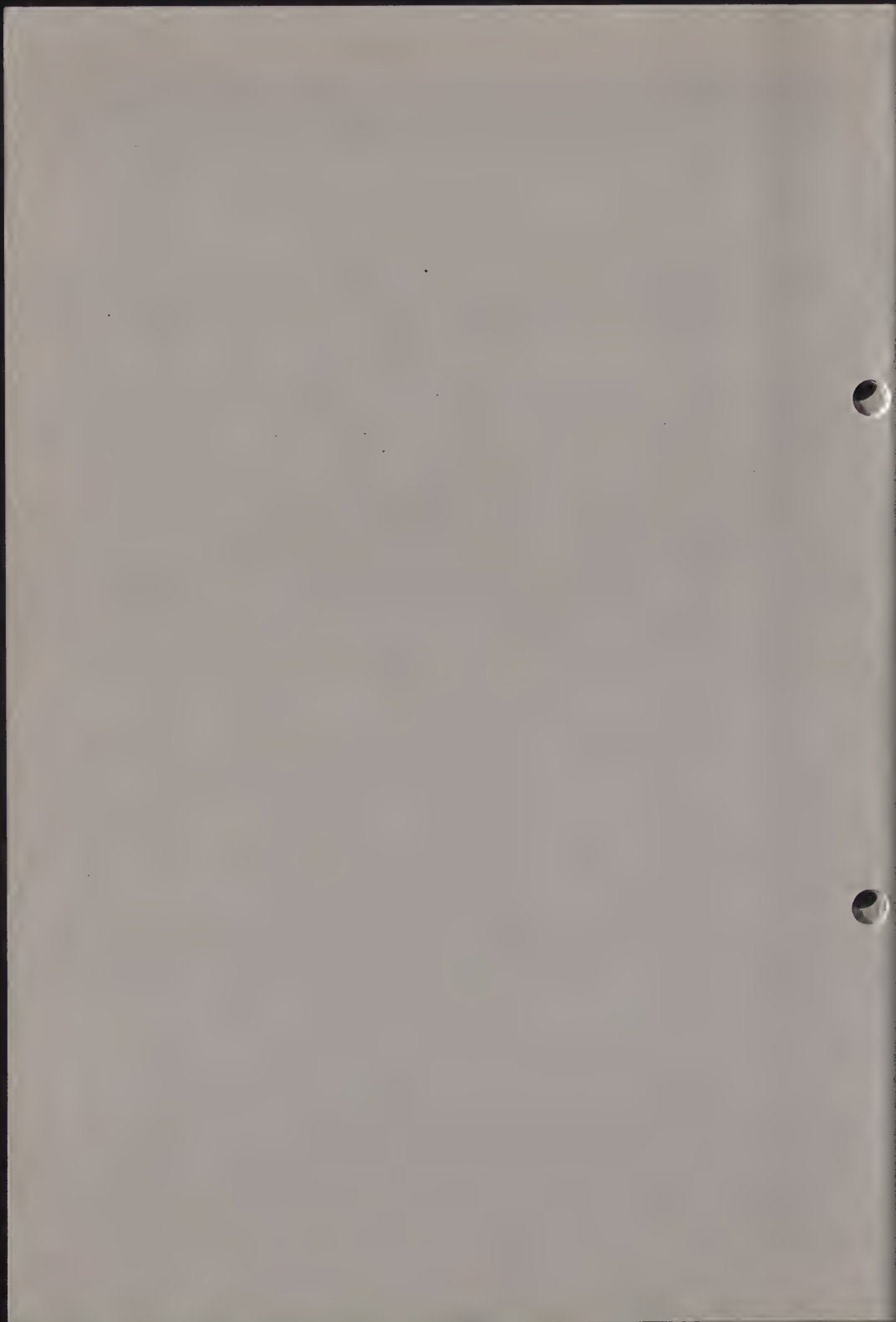
- 1) - Cennino Cennini. "Il Libro dell'Arte", cap.LIX e cap. LXXII.
- 2) - M.Matteini. "Ossidazione della Biacca in pitture murali. Metodi proposti per la riconversione del pigmento nelle pitture di A.Baldovini netti della Chiesa di S. Miniato (Firenze) Convegno sul restauro delle opere d'arte a dieci anni dall'alluvione. Firenze, XI, 1976 (it is in course of publication).
- 3) - J.W.Mellor. "A comprehensive treatise on inorganic and theoretical chemistry". Vol.XII, pag.684 segg.
- 4) - G.Charlot. "Selected constants-oxydoreduction potentials" pag.23 segg.

LA METHODE D'EXECUTION DES TRAVAUX
D'ENTRAINEMENT DANS LA TECHNIQUE DE LA
FRESQUE

A. Kouznetsov

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Peintures murales et
mosaïques



LA METHODE D'EXECUTION DES TRAVAUX D'ENTRAINEMENT DANS LA
TECHNIQUE DE LA FRESQUE

A. Kouznetsov

WCNILKR

10 Khrestyanskaya pl.

109172 Moscou

URSS

La méthode proposée d'exécution des fresques est destinée au perfectionnement des procédés de conservation des peintures déposées des murs. Son but principal est d'obtenir des plâtres ayant une composition nécessaire pour les travaux de laboratoire, d'entraînement et expérimentaux.

La déposition des fresques - c'est un moyen parmi les plus anciens de conservation des peintures pour éviter leur destruction. Cependant les procédés de la déposition des fresques du mur restent invariables depuis des siècles. Le perfectionnement de la technique suit, en général, deux directions: la sélection des matériaux pour la consolidation de la couche picturale et le choix de l'adhésif pour coller les fresques avant leur démontage. Avec cela tous les processus et l'expérience ac-

quise au cours du travail sur le mur sont souvent appliqués presque sans modifications dans la restauration de ce genre.

Mais si la technique de la déposition est assez bien élaborée, les opérations qui suivent, visant à assurer la longévité des fresques - la préparation à la transposition sur un nouveau support, la fixation sur ce support et la conservation ultérieure des fresques au cours des expositions exigent une grande expérience professionnelle. Mais pour acquérir cette expérience les spécialistes-débutants n'ont pas toujours à leur disposition des couches de plâtre nécessaires. C'est pour cette raison que l'aspect fragile du plâtre sans support entraîne chez eux le désir naturel de saturer d'avantage par des compositions de consolidation le côté face et le revers de la fresque, d'appliquer le nombre excessif de couches d'armature et de colles pour unir le nouveau support et les peintures murales. La sursaturation du plâtre et de la couche picturale qui en résulte devient souvent irréversible. Les fresques changent leur composition chimique et parfois même leur valeur artistique.

D'où la conclusion: le perfectionnement des procédés d'exécution des travaux sur les fresques déposées, l'étude des matériaux utilisés à ces fins et de tous les processus de la restauration pareille devraient être pratiqués sur les modèles-copies, faites sur une couche mince du plâtre, couverte de la peinture exécutée dans la tech-

nique de la fresque. Une question naturelle se pose : pourquoi précisément la fresque? La réponse est simple - lors de la consolidation des peintures sur un nouveau support on est obligé de coller le côté face. Une fois les travaux terminés, le collage est enlevé et avec cela la couche picturale risque d'être détremée. Par contre, la fresque permet de laver la peinture plusieurs fois avec n'importe quels solvants.

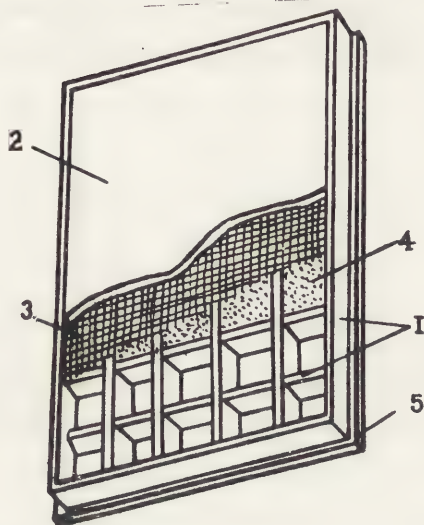
Le procédé traditionnel d'exécution des travaux d'entraînement dans la technique de la fresque est le suivant: on remplit une caisse de bois aux petits rebords d'une solution de chaux à plusieurs couches. Pour que la chaux ne se lézarde pas on y introduit des remplissages. Pour renforcer l'adhérence de la solution au bois on arme le fond de la caisse. On amène cette couche de plâtre à 50-60 mm d'épaisseur. Cela est nécessaire pour le maintien prolongé du plâtre en état humide.

La fresque obtenue par ce procédé est trop lourde et ne convient pas pour l'expérimentation. En même temps on n'a besoin de la couche épaisse du plâtre que pendant le processus du travail pour retenir l'humidité. Après la formation de la pellicule protectrice (CaCO_3) sur la surface de la peinture, les couches sous-jacentes perdent leur destination fonctionnelle.

Le procédé mis au point exclut tous ces défauts et consiste à l'application d'une couche mince du plâtre sur le matériau hygroscopique - sable, feutre, drap, etc,

d'où l'humidité monte dans la couche du plâtre pendant tout le processus de travail. Après la fin des travaux la couche hygroscopique est enlevée.

Pratiquement cela se passe comme suite:



On remplit le cadre parqué-
té avec le fond à bascule
par du sable humidifié.
Après avoir égalisé la sur-
face, on applique sur ce
sable une mince couche de
la solution de chaux (de 1-2
à 5-6 mm). Pour renforcer
le plâtre mince on pose une
toile entre cette solution
et le sable. La peinture est
faite par le procédé tradi-

tionnel - à l'aide des pigments dilués dans l'eau. Si le
travail prend beaucoup de temps, on humidifie périodique-
ment le sable. Après la fin des travaux on laisse le temp
pour que le plâtre se solidifie, on enlève le fond du
cadre, le sable s'écoule et la couche du plâtre est faci-
lement extraite du cadre. Si l'on utilise une toile de
séparation, on peut effectuer les travaux qui suivent
sans collage de la peinture. La chaux, ayant les proprié-
tés tenaces, s'adhère à la toile et est enlevée avec elle
Ainsi on obtient un collage original du revers de la
fresque.

La méthode décrite ci-dessus permet d'exécuter dans la technique de la fresque des croquis, des nature-mortes, des copies. Pour cela, avant de remplir la caisse par le sable, on colle une toile au parquetage du cadre à l'aide de l'adhésif résistant à l'humidité. Après l'écartement du sable et la fin des travaux la peinture reste fixée sur ce cadre. La réussite de cette méthode dépend de la chaux utilisée. Si l'on prend de la chaux fraîchement éteinte, la fresque risque ne pas réussir. L'eau s'infiltrant activement de la couche hygroscopique amène à la surface de la peinture une grande quantité de chaux diluée, ce qui entraîne la destruction de la couche picturale.

En dressant le bilan d'utilité de la méthode exposée on peut ajouter, que les fresques obtenues peuvent être utilisées dans les essais des adhésifs pour le collage des peintures avant leur démontage, dans les essais des solutions pour la fixation sur les murs des fragments des peintures déposées auparavant. Elle peut servir également pour déterminer la qualité des pigments et de la chaux, pour préciser l'utilité de leur emploi, pour mettre au point le processus de fixation des fresques sur un nouveau support ou bien, ce qui est particulièrement compliqué, leur montage sur le mur. Bien que la nécessité dans cette opération n'apparait que rarement, il serait utile d'acquérir de l'expérience dans ce domaine.



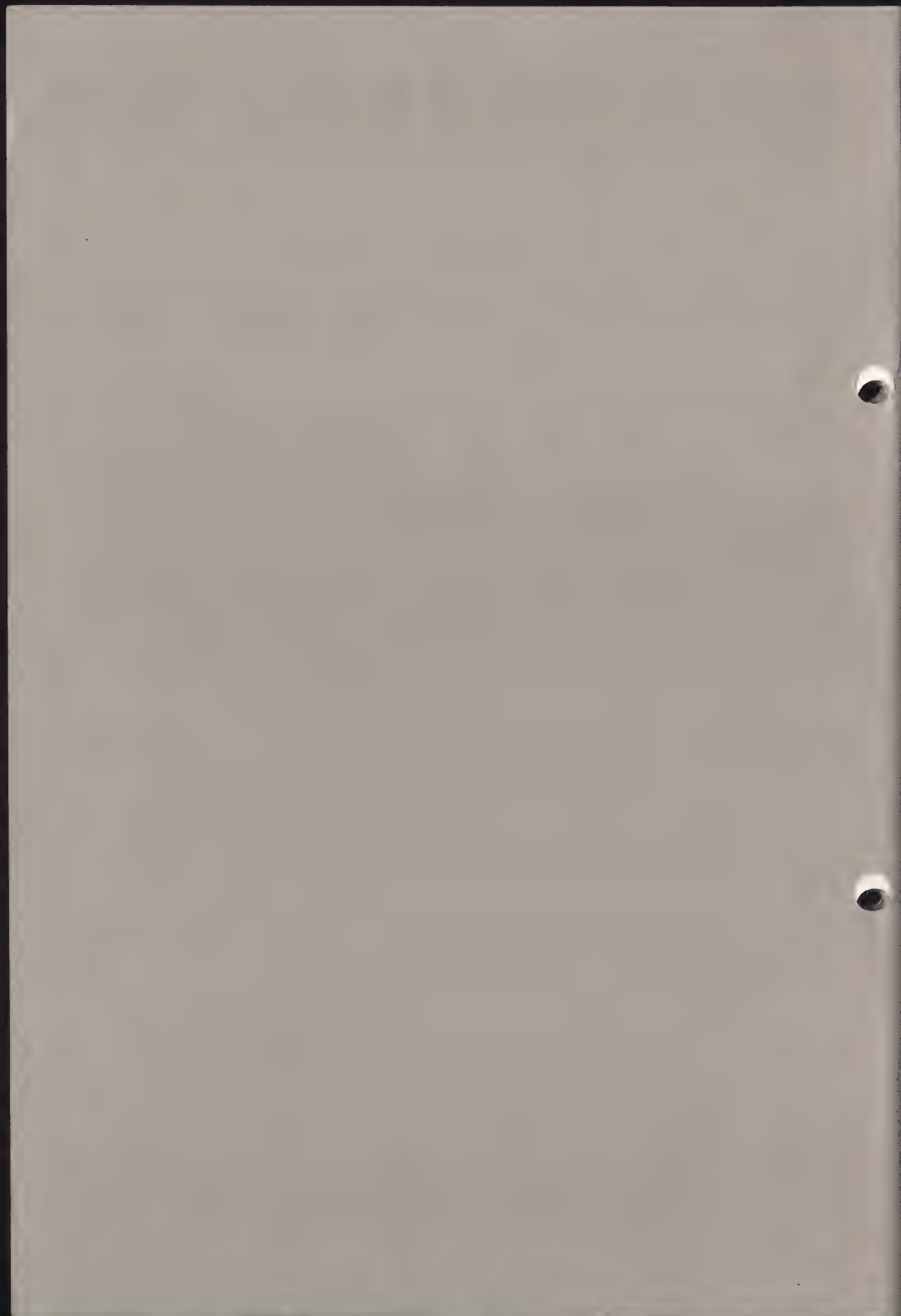
81/15/3

OBSERVATIONS AND METHODS OF CONSERVING ROMAN
WALL-PAINTING FRAGMENTS DUG OUT FROM THE
GROUND

Mathilde Schleiermacher

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Mural Paintings and Mosaics



OBSERVATIONS AND METHODS OF CONSERVING ROMAN WALL-PAINTING FRAGMENTS DUG OUT FROM THE GROUND

Mathilde Schleiermacher

Michaelweg 11
5000 Köln 50
Fed. Rep. of Germany

Wallpainting fragments from Roman times were put together like great puzzles. Some observations and results of the research of natural science concerning the technology of the mortar and the chemical analysis of the colours are described and different kinds of conservation are compared. Problems are standing out with solvents relating to the lime which is contained in the mortar in the case of pasting over tissues. By reason of whitening the colours it seems better, to find out a method of conserving this fragments only with little quantities of organic solvents and without pasting over tissues. If the fragments are hardened with ester of silicic acid, they can be assembled into a thin epoxid-mortar or polyvinylacetat-mortar and connected with honeycomb-sheets.

In Cologne fragments of Roman wall-paintings are no more a rarity in the meantime. The great post-war excavations brought to light more and more painted plaster from the Roman town. Mostly the fragments are found fallen down from the walls or in planed layers of Roman times; more rarely there are socle-stripes still in situ. A great number of fragments are strewn with small craters; they have been picked out by the Romans as preparation for fresh painting. After using the rooms for some years they showed wear and tear with colours effaced. The paintings had to be renewed and brought up to date. From the Roman Colonia Ulpia Traiana (Xanten) on the lower Rhine, we have examples with five painted plaster-layers one upon another. This lets us deduce, that the walls had been painted over for several times, finally there remained hardly anything of these. Frequently it became necessary to remove all the mortar for renovation and with the rubble the Romans could fill up a pit or a cellar, as it can be seen at the findings of the Limes castell Echzell (now Saalburgmuseum, Bad Homburg v.d.H.). From the Roman town Kempten-Cambodunum we also know planed layers. In Cologne the situation of the excavators is permanently

complicated, because short terms oblige to carry out so-called rescue operations. Often it is not even possible to take off all pieces of these fragile materials or to recover them in a whole. The Roman town is built over by medieval and modern buildings and often the painting-layers are troubled by later reconstructions. As elsewhere we must have a change of fortune, to put together a wall from such fragments, like a great puzzle. Our wall-painting-fragments are coming into the laboratory in very different conditions: frequently they are fragile and crumbly, the painted coating is powdery and the layer dissolves from the intonaco. Some are covered with lime-sinter. Others are relatively good preserved with two or three plaster-layers mutually in solid connection and the painted layer and intonaco compactly attached. In the case of the Cologne wall-paintings, the work is not carried out with so much display as for instance in the villa jovis of Tiberius at Capri, where one has followed the instructions of Vitruv, making six or seven layers of mortar. The Roman mortar is a mixture of rhine-sand and slaked lime. Flint in the size of seven to fourteen mm was added and found just beneath the surface of the painted coating. On the backside of the lime-mortar we have sometimes clay, put on by a kind of comb-spatula, mostly in zigzag courses obtaining a better adhesion on the walls. The paintings were designed in fresco-secco-technique, yet there is scarcely any doubt about it, especially since methods and research of natural science did confirm it. The painted great panels, the fries-stripes and also the greatfigured ground were made al fresco, on the wet mortar. Ornaments and little figurative details were painted later al secco with lime colour (lime-secco), glue-water-colour or lime-caseine-colour. This can be seen in particular on such painted parts, where the coated colour was mainly mixed with white of lime. Little spots are to see, where the colour has jumped off. The later painted colour is not so compact added to the ground like the ground-colour with the intonaco. Edgar Denninger, Stuttgart, succeeded in proving a reaktion of glutamin acid on samples of the red painting surface. This amino-acid occurs in animal glues, also in lime-caseine. Probably we might expect lime-caseine as a binding agent. Glue forms a very stable compound with the calcium hydroxide of the lime plaster. For the technical realisation "lime-fast" earth-colours were needed. All colour pigments except the black-ones were cristalline in the great candelabrum wall. Black was present as carbon in the form of soot or something similar. It was found red - red ochre; yellow - ochre, ferrum hydroxide; green - green earth, seladonite; blue - Egyptian blue, copper-calcium-silicate. The red paint layer is mixed with calcite cristalls due to an admixture of marble meal to the pigment. The admixed marble particles vary in size between 1,5 and 0,01 mm. By this admixture the paint was stretched and the layer of paint became more solid and more resistant. Certainly it

also contributes to the brilliancy which is so much admired on the Pompeian wall surfaces, and which is also present on the red fields of the painting of Cologne. The brilliancy is not however, to be explained by polishing with fine marble dust, as was at last claimed by W. Klinkert. L. and P. Mora found from experiments, that strong pressing and smoothening of the painting layer while it is still wet with trowel or spatula yields the brilliancy. In this process the colour pigments play an important role: earths like ochre, burnt ochre, green earth, white are based on clays. Already in pre-Roman times the effect of the brilliant clays had been discovered in the manufacturing of pottery. By pressing the surface tightly and as a consequence of the evaporation of the water the smallest particles get to the surface, tighten it and cause the brilliancy, because of the arrangement of the particles of clay minerals in parallel layers double refraction is perceptible. The black frieze of the Cologne paintings did not glitter. The black paint layer is extremely thin, only 5 - 10 μm , the red one on the other hand 200 - 500 μm . The lubricant, e.g. caoline, which also gave brilliancy to the soot colour would have had to be added beforehand, because the clay components are lacking in the black colour. If the spectrum of the X-ray analysis showed calcium and silicium even in the black colour, the underlying layer of fine plaster could have been registered because of the thinness of the paint layer. The scientific proof for the correctness of the explanation found for the brilliancy of the painting layer of Roman mural paintings by Mora lies in the proportion of silicium and aluminium contained in clays (water bearing aluminium-silicate) and hence also in clay based colours. Portions of silicium and aluminium could be ascertained in paintings of Pompei, of Kasanlak (Bulgaria), of Münsing and Hölstein (Switzerland), and of Cologne, - in the Cologne paintings in the red and green painting layers. In the ochre there were caolinite, calcite, quartz, and clay minerals.

For other wall-painting finding-complexes are analyses in course.

The conservation has to begin with examinations concerning the condition of the fragments. Mostly, we have first to solidify the Roman mortar by ester of silicic acid. Only then, it will be possible to remove, if necessary, by means of a corund disc the incrustation of lime-sinter. The paintings often show it on many spots. The incrustations have firmly coalesced with the painting layer. The cleaned fragments will be put together in their positions and plane level in prepared cases with a filling of Vermiculith (mineral, product of weathering of different kinds of glimmer). This material is much lighter than sand, so turning the cases to the backside is easier. In the state, of having fitted all pieces possible together, we fabricate a reconstruction drawing. After fixation of the painting layer with Para-

loid B 72 diluted in Nitro (mixture of nitrobenzene), the fragments have been pasted over twice with trevira-tissue, first a fine one and then a coarse one, also with Paraloid B 72 in stronger consistency. The painted layer was now so safely protected against fracture, that after turning the cases, we could grind off the Roman mortar till a thickness of 8 mm. This may best be done with the aid of an ultrasonic chisle (KLN-Ultraschall GmbH, Weinheim). For a second hardening of the antique plaster from the reversed side, we used Primal AC 33, an acrylum emulsion (Rohm & Haas, Philadelphia). The 4 mm thick layer of plaster that had been laid on for equalisation consisted of three portions quartzsand and one portion lime from a lime-pit and 10% of a mixture of Mowilith D 50 and D 025 in equal portion. Over the dried plaster we pasted a stronger armouring cloth. This may, if needed, be solved with nitro-dilution, so that the restoration remains reversible. Subsequently it was connected with the light-weight panels from honeycomb-aluminium (Aerolam-F-Board Panels, Ciba-Geigy AG, Basel). After hardening, the mounted paintings were turned over and hanged into profiled steel frames. The next operation consisted of laying open the image side. Cotton soaked with nitro-dilution was distributed over the cloth pasted over the painting surface which we had before-hand carefully prediluted, and the entire surface was covered over night with polyethylene foil. On the following day, we could take off the cloth easily and in the case of the strengthened fragments without loss of paint. Otherwise, we learned on the wall with a hunting-scene - there were some fragments not undergone the treatments of consolidation by ester of silicic acid - that this is necessary in most cases, for we had some little losses of colour on it, when we were removing the tissues from the painted layer. For filling the missing places we used now a plaster only from lime and sand. To make the filling easier, resp. to protect the painting, we used Mowiol (PVAL) on the painted fragments. But this seemed to be a disadvantage, for we had the difficulty of a contraction between Mowilith from the ground-mortar and Mowiol. In both, Mowilith-dispersion and Mowiol is included polyvinylalcohol. We saw the colours getting darker, but we could dissolve it with water.

On fragments, found in Echzell (now Saalburgmuseum, Bad Homburg v.d.H.) we observed now disadvantageous results after removing the tissues, probably there was a more advantageous bedding in the earth, respectively the chemical ingredients of the surrounding ground did not damage the painted fragments.

We are going to consider the pros and cons:

Echzell (Saalburgmuseum, Bad Homburg v.d.H.)

Wallpainting with mythological scenes, ca. 3,17 x 1,30 m, high of the reconstruction 2,22 m.

Fragments put together without treatment by ester of

silicic acid. The structure of the Roman mortar was good preserved. The painting layer showed great spots of sinter incrustation. It was not possible to remove them totally, they only have been softened. Fixed and pasted over with Paraloid B 72, diluted in Nitro. The Roman mortar was thinned down to 8 mm with rasps and chisels. Backside fixed with Primal AC 33. Mounting in mortar with polyvinylacetate (Mowilith): 3 parts sand, 1 part lime, 10% Mowilith D 50 and D 025 in equal portions. Assembling on honeycomb paper-panels, prepared with glass fibre and Araldit.

Köln 1. Candelabrum-walls.

Wallpaintings mostly with motifs from the dionysian world, with great red panels and candelabrum stripes, long ca. 8 m, wide 4,50 m, high ca. 2,80 m, reconstruction ca 45 qm.

Fragments from the great excavations around the cathedral put together after treatment by ester of silicic acid Laosin B. Fixed and pasted over with Paraloid B 72. Roman mortar thinned down to 8 mm with a cutting-off disc. This gives much crumbling into dust and the possibility of hairline crack. Assembling like Echzell.

Köln 2. Hunting-scene.

Great figured hunting scene 1,64 x 2,42, panther 1,54 x 1,40 and tendril 2,00 x 0,31 m; Fragments were coming from the same excavation and room like the candelabrum-wall. Put together partial without treatment by ester of silicic acid. Mortar thinned down with ultrasonic-chisel (KLN-Ultraschall GmbH, Weinheim). That has been more careful than the work with a cutting-off disc. Fragments without treatment by ester of silicic acid had a somewhat lesser connection between the painted layer and intonaco, further there is the possibility of a contraction between Mowilith and Mowiol in the case of utilisation of PVAL, may be also the danger of penetration of Mowilith into the painted layer.

Trier - Landesmuseum. Wallpaintings from excavations in the Roman town, partially found in situ.

Treatment by ester of silicic acid (Hermetique conservans, Fa. Bauchemie, Garmisch-Partenkirchen). Fixed and pasted over with Mowilith 35/73 diluted in äthylacetate. Removal of the Roman mortar till down to the intonaco of 1/2 - 2 mm. Mounting in mortar with polyvinylacetate without lime: 4 parts Mowilith (3 parts D 025 and 1 part D 50), 8 parts water and sand till it was good to smooth. This mortar has been applied only from the backside in a layer of 1-2 mm and was reinforced with a cotton-netting, stabilised with a wooden cadre, or one from aluminium-pipe. Neither Mowilith nor lime penetrates through the painting into the frontside. To make the painted layer plane, it was a little bit pressed from the backside. That makes possibly little cracks. It must be seen as operation to separate the whole mortar from the intonaco.

Trier - Diözesanmuseum. Wallpainting-fragments from the ceiling of the Constantinian palace.

The fragments have been hardened with Paraloid B 72, diluted in Toluol, which penetrated through the whole pieces. Now pasting over a tissue. The mortar has been removed to ca. 12 mm and then the fragments were assembled on chip-panels.

In our special case, it seems to be better, finding out a technique to assemble the fragments without pasting over tissues, except they could not be salvaged in another way. May be, it's possible to find out a combined method, with only the advantageous elements of our experiences taken.

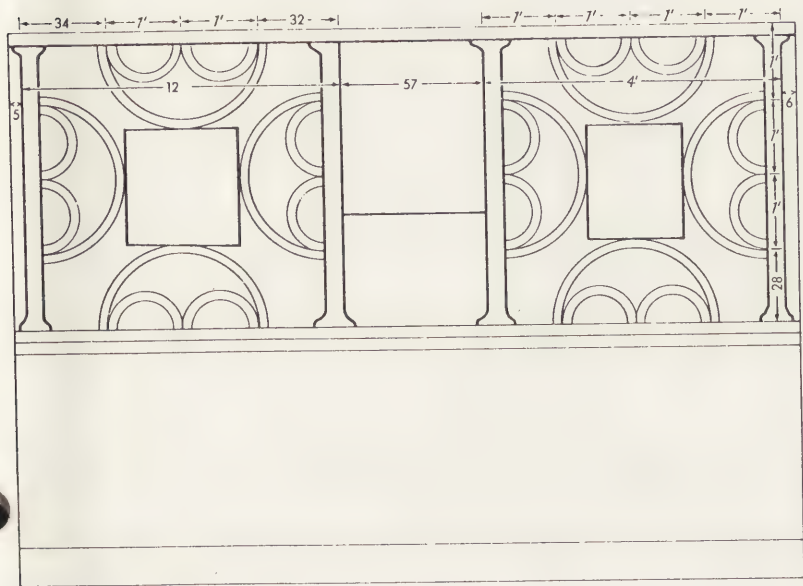
The following difficulties are to be seen, if wallpainting fragments are dug out from the ground. There is the soil-condition, that means different chemicals around the fragments in the ground, which may have penetrated into them. Therefore they differ in resistance and stability. They are also not of the same heights. First they are to clean and to dry. Sometimes it's necessary to harden them before cleaning. The cleaning must be done as dry as possible, for there is the danger of penetration of lime to the frontside which would make a white film.

Observations on our material have shown, that the pasting over with Paraloid B 72 or with Mowilith will change the characteristics of the paintings much more than the treatment with ester of silicic acid. It produces a skin, that is more solid than the underground of the intonaco. The paintings do not have any more the impression of a crystalline wallpainting. Because the solvents have whitened the colours while removing the pasted tissues, it's necessary, to give enough of the diluted polyvinylacetate or polyacrylate back to the painted layer.

We make tests to reinforce the fragments with Funcosil (ester of silicic acid from Remmers Chemie, Wermelskirchen) and to thin them down with the ultrasonic chisel without pasting over tissues. That it is practicable to assemble the fragments, can be seen at the restorations in the Diözesanmuseum, Trier by W. Steffny. The not known component is the possible chemical difference of the fragments. To equalise the surface, we have to put the fragments into a two mm layer of mortar with polyvinylacetate, e.g. Mowilith. The missing parts, we can fill on with a mortar from lime and sand. Probably we can get a mortar very similar to the original Roman by using the material we scraped from the original fragments. Otherwise a filling that consists of Vermiculith, quartzsand, Mowilith and lime it's weight could be reduced (employed for mosaikpanels in the British Museum, London by P. Shorrer).

Literature

- P. et L. Mora et P. Philippot, La conservation des peintures murales, Bologna 1977.
- W. Klinkert, Bemerkungen zur Technik der pompejanischen Wandmalerei, Römische Mitteilungen 64, 1957, 111-148.
- W. Noll, L. Born, R. Holm, Chemie, Phasenbestand und Fertigungstechnik von Wandmalereien des römischen Köln, Kölner Jahrb. 13, 1972/73, 77 ff.
- M. Schleiermacher, Zur Restaurierung der römischen Wandmalereien der Domflächengrabung 1969/70, Kölner Jahrb. 14, 1974, 96 f.
- R. Wihr, Erfahrungen bei der Bergung und Konservierung römischer Wandmalereien und Mosaiken, Arbeitsblätter für Restauratoren 1, 1968, Gr. 7, 1-10.



Echzell, system of the Roman wallpainting with mythological scenes: in the middle-field Fortuna and Hercules, left side, Theseus and Minotaurus, right side, Ikarus and Dädalus. Pelta-shields are surrounding the pictures of the side-fields.
M 1:25, published in Germania 46, 1968, 40 ff.



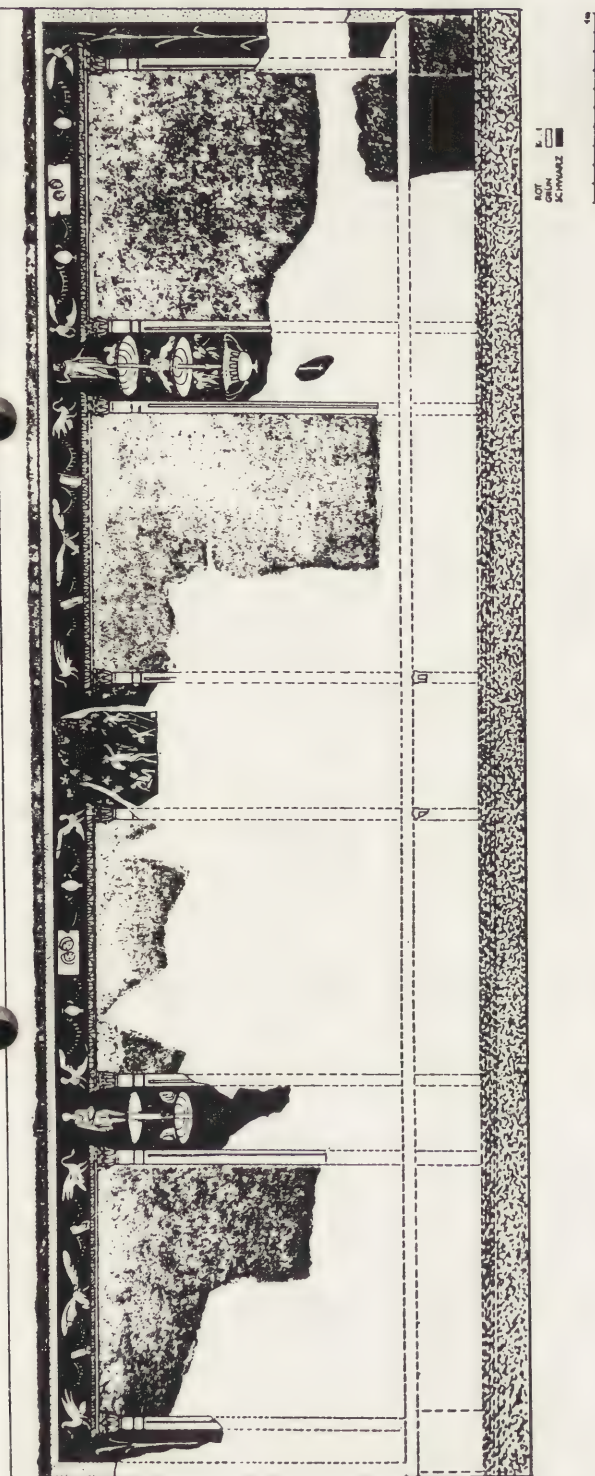
Panther

0 10 20 30 cm

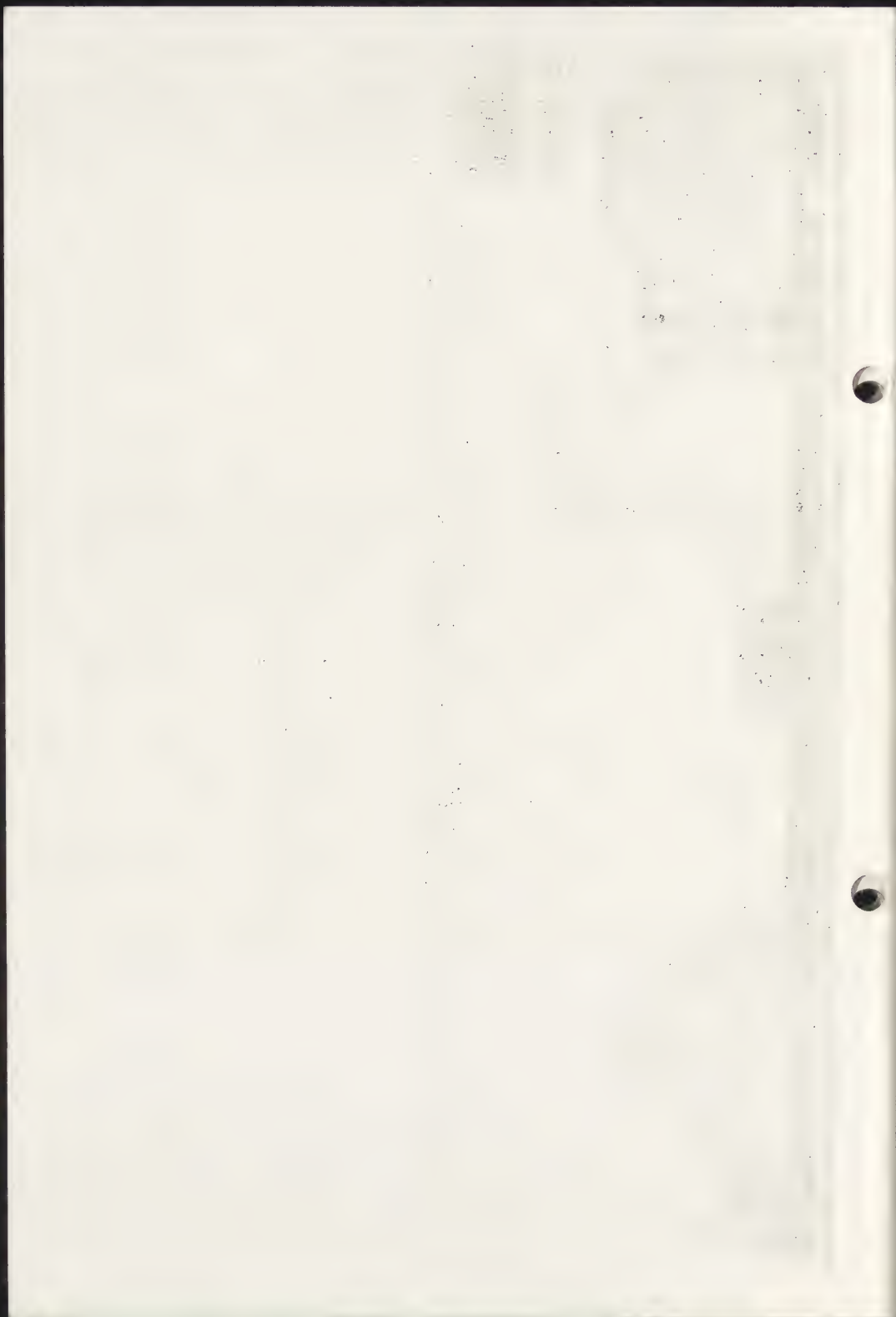


Hunting-scene,- both excavated 1969, Cologne Cathedral, southside. M 1:15

0 10 20 30 cm



Cologne, Candelabrum-wall with great red panels, black frieze and candelabrum-stripes with dionysian motifs, in the middle field a vintage scene. Excavated 1969, Cologne, Cathedral, south-side, 8 m x 2,80 m. Drawing A. Becker, published in *Kölner Jahrbuch* 13, 1972/73, 65 ff.
Conservation of the wallpaintings from Echzell and Cologne, M. Schleiermacher.



81/15/4

CRITERES ET RESULTATS DANS LA RESTAURATION
DU CIBORIUM DE S.AMBROISE

Pinin Brambilla Barcilon

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Peintures murales et
mosaiques



CRITERES ET RESULTATS DANS LA RESTAURATION DU CIBORIUM
DE S.AMBROISE

Pinin Brambilla Barcilon

Via San Senatore 2
Milano
Italie

Résumé

Le ciborium de S.Ambroise à Milan est au centre d'une problématique visant à établir une chronologie plus précise aussi bien de la structure architectonique que de la décoration plastique.

L'unique point de référence pour lequel tout le monde est d'accord concernant les études sur le ciborium, est l'autel d'or, dont la commande fût faite à Vuolvinio, par l'évêque de Milan Angiberto, vers 830-840.

Autour de ce point de départ on a tracé différentes interprétations sur le ciborium surmontant l'autel: entre autre il y a celle désormais vetusse, qui considère l'oeuvre comme étant contemporaine à l'autel et celle qui la situe, avec des solides arguments, à l'époque d'Othon ou celle encore qui la date plus tard, à la fin du XII siècle.

Des précisions plus approfondies par les spécialistes n'ont pas été possibles jusqu'à présent, en partie à cause de l'absence de vérifications directes sur l'oeuvre, à savoir des enquêtes scientifiques, des examens et des sondages stratigraphiques.

Nous souhaitons que grâce aux dernières interventions faites sur l'oeuvre la critique puisse trouver quelques certitudes.

Enquêtes sur les matériaux et les procédés techniques de l'architecture

La maçonnerie du ciborium est composée en général de matériaux de récupération: de briques ébréchées de dimensions irrégulières, reliées par une grosse couche de

mortier granuleux (de la chaux, du sable grossier et de l'argile). La couverture se présente avec deux structures superposées: une voûte à arêtes avec des nervures à section rectangulaire et une deuxième à couverture à pignon. Dans l'interstice, rempli avec des fragments irréguliers, on trouve une niche, en correspondance avec l'image de S. Ambroise: probablement un reliquaire. Le lambris de l'organisme architectonique se présente différemment. Les façades extérieures des flèches sont lambrissées avec une première couche de mortier (de l'argile mélangée à la chaux avec un liant de matières organiques) et avec une seconde couche d'un mélange d'argile plus fine et bien polie; nous trouvons un lambris du type d'enduit fin (cacciopesto) dans l'extrados de la petite coupole, dans la zone périmétrale plate.

Enquêtes sur les décorations en stuc

Technique. Les zones destinées à la décoration apparaissent délimitées avec un instrument pointu et par de rapides traces gravées sur l'enduit du support; ces zones où l'on ébauchait par la suite des sinopia aux contours rouges et noirs (notez dans les pinacles les traces de sinopia sur les mains, sur les clés du Christ et dans les contours des figures).

Le modelage en relief était obtenu avec des premières couches superposées et plates, qui étaient galbées dans la dernière couche avec force et finesse, par des instruments pointus, et accrochées au support en utilisant de gros clous. Il est probable que le stuc qui a la particularité de se sécher rapidement, était gardé en condition de malléabilité en travaillant pendant les saisons chaudes ou bien en ajoutant du gypse réchauffé. Ce qui explique l'opération de stratification des décorations.

Composition du stuc: d'aspect légèrement rosé, dû, selon les analyses chimiques, à un mélange composé surtout de gypse, avec de petites quantités de carbonate de chaux, de traces de sable, d'argile et d'ocre rouge.

Il est probable qu'un tel mélange ait été employé aussi bien pour rendre la surface de l'oeuvre plastique moins poreuse, que pour servir de base à la coloration.

Enquêtes pour la découverte de la polychromie originale

Sur la base de traces de couleur minuscules trouvées dans les sillons des reliefs et dans les cadrages des

fonds, nous pouvons penser que la polychromie originale visait à être un ensemble décoratif organique, étendu non seulement sur les parties plastiques en relief mais aussi sur les fonds. Nous en avons une preuve grâce aux traces de sinopia que l'on peut relever sur les fonds des parois nord et sud des flèches, et aux fragments de fresques autour des lacunes de couleur du XIV siècle sur la partie inférieure gauche de la flèche nord et aux autres traces sur la paroi nord. Les décorations originales retrouvées ne sont pas seulement de simples motifs d'équarissage géométriques, mais aussi des bandes florales et des motifs de décoration autonome, comme le dessin d'une fleur trouvé près de la main d'une figure féminine. La décoration originale semble presque complètement perdue, probablement à cause des interventions successives rendue nécessaires au cours des siècles à cause d'une dégradation progressive.

Voici les pigments identifiés dans la composition picturale:

2 types de pigments blancs: blanc de S. Jean et carbonate basique de plomb (céruse)

1 type de pigment noir: noir de charbon

1 type de pigment bleu clair: lapis-lazuli

1 type de pigment brun: terres brunes

2 types de pigments rouges: terre rouge et cinabre

2 types de pigments verts: malachite et terre verte

2 types de pigments jaunes: orpiment et ocre

Les enquêtes et les localisations des traces de polychromie originale nous portent à conclure que la décoration des flèches est l'oeuvre de plusieurs personnes, même si elle est unifiée par la bande rosée florale qui délimitait les périmètres. De plus, les flèches nord et sud apparaissent assez semblables aussi bien dans le modelé que dans le chromatisme à tons éteints et foncés. Une technique picturale de clair-obscur, basée sur les variations d'intensité de couleur, soulignait la profondeur des plis des vêtements, en en accentuant les volumes. La même technique peut être relevée sur les flèches arrières et frontales et semble être l'oeuvre de deux mains différentes, toutes les deux orientées vers l'emploi de couleur plus intenses et variées.

Le résultat des examens porte à croire que le ciborium était à l'origine complètement polychrome. La couleur avait la fonction de relier le relief plastique, c'est à dire la forme, au plan du support donnant ainsi unité chromatique à l'ensemble.

Méthode de restauration

Elle est basée sur trois points fondamentaux:

- 1) l'identification des transformations et de la modification de la structure
- 2) l'évaluation de l'importance historique et documentaire des transformations
- 3) le choix des interventions et du type de conservation

Un premier nettoyage fit apparaître une couche chromatique très intense du XIX siècle visant à une réfection grossière du modèle plus ancien. Des prélèvements d'échantillons et des sondages en profondeur révélèrent les couches au-dessous, ce qui permit d'établir les critères à adopter: renoncer aux "repeints" du XIX siècle pour faire émerger la pellicule picturale du XIV siècle, que les enquêtes confirmèrent comme étant la plus appropriée, à cause de son état de conservation, qui assurait une unité homogène et une fidélité historique au ciborium.

Ayant établi ces critères, on a pu constater à travers les prélèvements de la surface peinte et les analyses stratigraphiques chimio-physiques, ainsi que les examens faits au microscope que l'aspect actuel du monument était complètement déformé par rapport à l'originale, puisque la superposition de couches de différentes matières avait aplati la vigueur des volumes, le caractère incisif du modelé, le naturel des traits dans les visages des personnages.

Les examens confirmèrent en outre les interventions précédentes et les époques:

- 1) 1945-50: de petits stucages et retouches sur l'or au moment du déplacement des protections anti-bombardement
- 2) 23.10.1873: des interventions étendues à tout le ciborium
- 3) juillet 1836: date inscrite sur le placher de la calotte et sur la contrefaçade frontale
- 4) XIII siècle: des interventions sur la flèche frontale, sur la décoration des arc-doubleaux et sur les nervures
- 5) XIV siècle: des interventions sur les parois des flèches
- 6) avant le XIV siècle: des réfections localisables sur les pilastres
- 7) 1200-1300: contour des reliefs plastiques avec du minium.

Les travaux de restauration actuels ont pu établir et saisir aussi bien l'entité et la technique que la signi-

fication de chaque intervention par rapport à l'évolution de la culture artistique pendant le siècle. Dans ce sens la flèche frontale est particulièrement exemplaire.



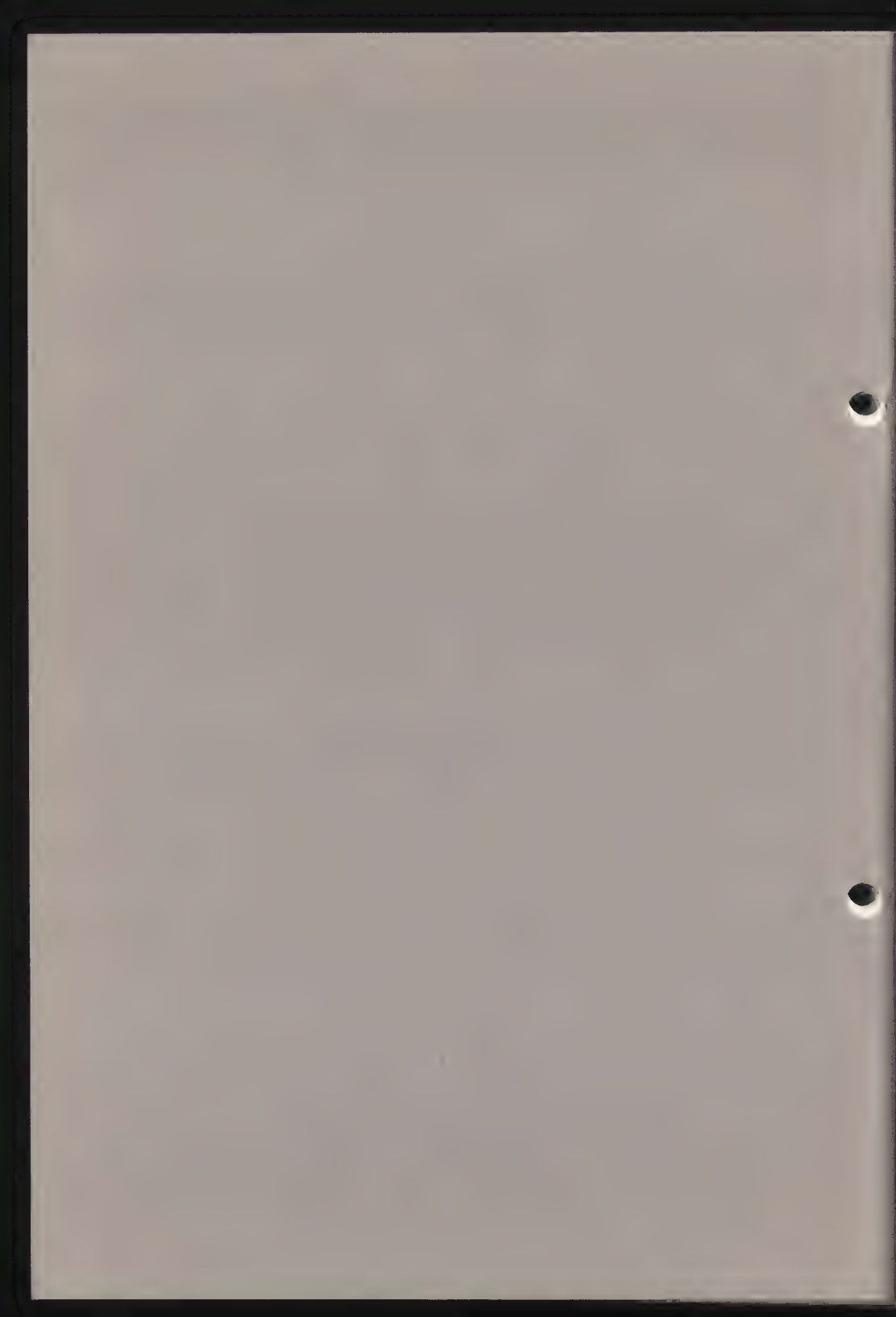
81/15/5

MICROORGANISMS AND ENVIRONMENTAL POLLUTION
AS DETERIORATING AGENTS OF THE FRESCOES
OF THE MONASTERY OF "SANTA MARIA DE LA
RABIDA", HUELVA, SPAIN

C. Saiz-Jimenez and R.A.Samson

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Mural Paintings and
Mosaics



MICROORGANISMS AND ENVIRONMENTAL POLLUTION AS DETERIORATING
AGENTS OF THE FRESCOES OF THE MONASTERY OF "SANTA MARIA DE LA
RABIDA", HUELVA, SPAIN

C. Saiz-Jimenez and R.A.Samson

C. Saiz-Jimenez
Centro de Edafologia y Biologia Aplicada del Cuarto
Consejo Superior de Investigaciones Cientificas
Apartado 1052
Sevilla
Spain

R.A.Samson
Centraalbureau voor Schimmelcultures
P.O.Box 273
Baarn
the Netherlands

ABSTRACT

A study was made of the microbial deterioration of frescoes at the monastery of "Santa Maria de la Rabida" in Huelva, Spain. Main deterioration signs are efflorescence, dark stains and scaling of the surface layer of the picture. Efflorescence is caused by calcium sulphate (gypsum) and minor amounts of calcium chloride, sodium chloride, potassium chloride, nitrates and silicates. The microbial population is mainly composed of the fungi *Cladosporium sphaerospermum*, *Engyodontium album* and *Aspergillus versicolor* and the bacterium *Micrococcus luteus*. A predatory mite, *Tyrophagus palmarum* was also found on the microorganisms. It is suggested that a close link exists between the biodeterioration of frescoes and environmental pollution, although wall humidity can be considered the starting point of deterioration.

Weathering of mural paintings is quickened by well known environmental agencies such as temperature, humidity and salt concentration. In addition, the microbial population may also contribute to the decay.

Microbiological aspects of mural paintings have been discussed in several papers, the role of fungi in degradation being stressed. The influence of environmental factors on fungal behaviour have also been pointed out (Savulescu and Ionita, 1971; Ionita, 1973;

Bassi and Giacobini, 1973; Tiano and Gargani, 1976).

In this paper a study is made of the role of fungi in the deterioration of the frescoes at the monastery of "Santa Maria de la Rabida" in Huelva, Spain, and the influence of the environmental pollution on the microbial growth.

The monastery was built in the 14 and 15th centuries and is considered the cradle of the Discovery of America. The frescoes which adorn the porters lodge were executed by Daniel Vazques Diaz in 1929-1930 on a mixture of sand and lime and cover the entrance and the four inner walls of the room. They depict the so-called "Poema del Descubrimiento", a Discovery allegory.

The decay of the frescoes began about 10 years ago, and coincides with the settlement of industrial plants in the area. At present three of the walls are badly decayed. Two well-differentiated types of deterioration can be observed: a wide zone consisting of white efflorescences and other whitish stains in the shape of drops of condensation, particularly on those walls whose external surface are exposed to rain; and a zone with green to black stains (figures 1 and 2). Both zones were studied separately.

Efflorescences have been considered to be of either chemical origin, due to migration and crystallization of soluble salts (Mora et al., 1977), or biological, due to bacterial growth (Lazar, 1971; Bassi and Giacobini, 1973). Electron dispersive analysis of the whitish powder by X-rays (EDAX) showed the presence of S, Ca and Si as major elements and Cl, Na, K, Mg, Al, P and Fe as minor elements. Scanning electron microscopy (SEM) interfaced with EDAX showed that most of the inorganic particles consisted of calcium sulphate, with minor amounts of calcium chloride, sodium chloride, potassium chloride, silica and silicates. As N cannot be analysed with the equipment used, nitrates were not observed, though the presence of N was proved by spot test analysis (Feigl, 1958).

The saline efflorescences were easily removed by gentle brushing, but the colours of the paintings were denatured and had lost their original intensity, thus suggesting alteration. No detachment or scaling could be observed in these zones.



Figure 2. Fresco with dark stains and scaling

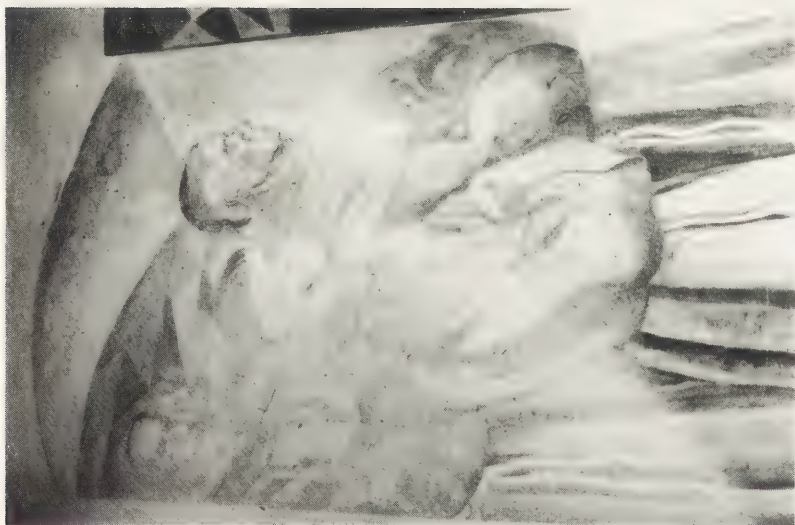


Figure 1. Fresco with efflorescences .

Efflorescence samples collected between May 1979 and July 1980, during different seasons, were employed for microbiological analysis. The methods used were those described by the Group of Biology of the Conservation of Stone (1976). Estimation of the most-probable-number of fungi ranged between 5.000 and 8.000 per gram of sample. Czapek-Dox-agar, potato-dextrose-agar and malt-agar were employed as culture media for fungal isolation. The species of isolated fungi are shown in table 1. *Cladosporium sphaerospermum* represented about 75% of isolates, and together with *Engyodontium album* and *Aspergillus versicolor* it accounted for 90% of total number of fungi isolated.

It appears that saline deposits may provide a suitable habitat for fungi, especially for the above-mentioned species. *A. versicolor* was only isolated from the last sample and replaced *E. album* as the second most important fungus in the efflorescence, thus denoting a variation in environmental conditions and/or substrate, the last summer being more favourable for the growth of *Aspergillus*.

One of the feature which promotes the survival of certain fungi, is a capacity to tolerate the harsh environment created by the presence of high osmotic substances. Tresner and Hayer (1971) reported that *Penicillium* and *Aspergillus* species were outstandingly more resistant to NaCl than any other studied organisms. From 124 species of *Penicillium* 97 could tolerate 20% NaCl and 70 survived at 25% or greater concentrations. The aspergilli appeared to be somewhat less tolerant; nevertheless, 56 species could withstand 20% NaCl and 35 survived at 25%. It is interesting that of 15 strains of *Penicillium chrysogenum*, a species also found in frescoes, all were tolerant to 25% or greater concentrations of NaCl.

Gargani (1968) studied the damage to frescoes in florentine churches during the years 1961-1965. Many *Penicillium* species were identified: e.g. *P. citrinum*, *P. commune*, *P. camemberti*, *P. purpurogenum*, *P. restrictum*, *P. frequentans*, *P. decumbens*, *P. thomii*, *P. canescens*, *P. janthinellum*, *P. chrysogenum* being *P. decumbens* the most frequent. *Aspergillus* species were seldom found. However, *Cladosporium* attack has been said to be the most serious form of

TABLE 1

Fungi isolated from efflorescences during the period May 1979 to July 1980 (four samplings).

Species	isolates
<i>Cladosporium sphaerospermum</i> Penzig	177
<i>Engyodontium album</i> (Limber) de Hoog	26
<i>Aspergillus versicolor</i> (Vuill.) Tiraboschi	10
<i>Penicillium brevi-compactum</i> Dierckx	3
<i>Penicillium citrinum</i> Thom	2
<i>Penicillium decumbens</i> Thom	2
<i>Acremonium charticola</i> (Lindau) W. Gams	2
<i>Phoma glomerata</i> (Corda) Wollenw. & Hochapf.	2
<i>Alternaria alternata</i> (Fr.) Keissler	1
<i>Arthrimum</i> -state of <i>Apiospora montagnei</i> Sacc.	1
<i>Botrytis cinerea</i> Pers. ex Fr.	1
<i>Chaetomium elatum</i> Kunze ex Fr.	1
<i>Chaetomium</i> sp.	1
<i>Cunninghamella echinulata</i> (Thaxter) Thaxter	1
<i>Penicillium nigricans</i> Bain.	1
<i>Penicillium raciborski</i> Zaleski	1
<i>Penicillium verrucosum</i> var. <i>cyclopium</i> (Westling) Samson, Stolk & Hadlok	1

TABLE 2

Fungi isolated from dark stains during the period May 1979 - July 1980 (four samplings).

Species	isolates
<i>Cladosporium sphaerospermum</i> Penzig	110
<i>Engyodontium album</i> (Limber) de Hoog	12
<i>Penicillium chrysogenum</i> Thom	1
<i>Penicillium frequentans</i> Westling	1

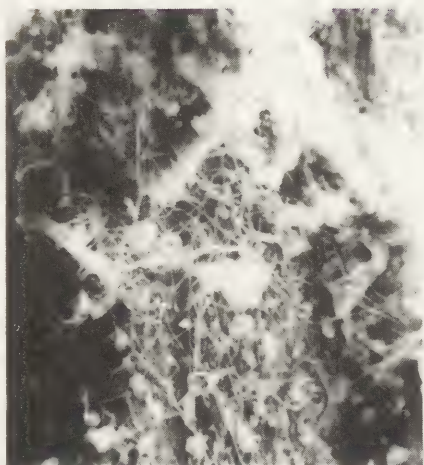


Figure 3. Fungal growth on fresco. x 850



Figure 4. *Cladosporium sphaerospermum* hyphae and conidia. x 4.300



Figure 5. Hyphae on gypsum crystals. x 4.300



Figure 6. Conidium and hypha on gypsum crystals. x 4.300

deterioration of fresco paintings in modern times (Giocobini and Lacerna, 1965).

Cladosporium species have been reported to cause changes in frescoes, sometimes resulting in irremediable damages. The fungi may either produce superficial, variously coloured stains, which denature the chromatic and aesthetic aspects of paintings, or serious alterations by hyphal penetration or degradation of substrates resulting in initial detachment of fragments (Giacobini and Lacerna, 1965; Bassi and Giocobini, 1973; Ionita, 1973).

In fact, close to an efflorescence zone *C. sphaerospermum* was found to produce dark stains on a well-differentiated region of one of the paintings studied. *E. album* and two penicillia were isolated with *Cladosporium* in a few cases (table 2). The attack of this fungus is characterised by small to moderately large green, olive green or black stains, which are irregularly distributed and incrustated among the sea sand grains of the rough fresco surface (figure 2). The hyphae penetrate into the picture layer and the stains cannot be removed with a scalpel. Scaling is evident. Detachment of stains also implies removal of a portion of substrate to which they are firmly adhered (figure 3).

A SEM micrograph from dark stains showed a well-developed mycelium with septate, abundantly branched hyphae; conidiophores arising laterally and terminally from the immersed and aerial hyphae, growing in different directions, smooth, irregularly septate, with rather short prolongations with more or less pronounced inflations where conidial chains were attached; conidial chains very fragile, breaking up readily into units, leaving only naked stumps. The developing mass is loose, with hyphal tip growth, which in some instances approach as yeast-like budding. Conidia developing in acropetal succession as blown-out ends at the apex of single or branched conidiophores, which then do not increase in length. Conidia are 2-celled, smooth, oval, cylindrical, constricted at the septa (figure 4).

Damage due to *Cladosporium* species, such as *C. herbarum*, has reported by Savulescu and Ionita (1971) and Ionita (1973) on Ruma-

nian mural paintings. *C. herbarum*, *C. sphaerospermum* and *C. clado-sporioides* and a few unidentified species have been isolated from Italian frescoes (Giacobini and Lacerna, 1965; Bassi and Giacobini, 1973; Tiano and Gargani, 1976).

Of the other species recorded, *Phoma glomerata* is particularly interesting in that it was considered to be specific and constituted the alarm signal of exterior water-thinned paint films degradation (Drescher, 1958). Ionita (1973) applied this statement to frescoes biodeterioration. In what extent it may be valid is a matter to be discussed.

Many factors may influence fungal ecology in frescoes. According to Garret (1963), the physico-chemical characteristics of a habitat determine the kind of community, but the precise composition will be depend on species competition. Thus, the first selecting factors which determine the nature of a community will be type of a substrate and the prevailing environmental conditions. These factors will select from the organisms available, favouring some at the expense of others, and excluding some altogether (Park, 1968).

The original walls were built from bricks and mortar as support with a rendering of sand and lime. The pigments chosen for the fresco were reported to be inorganic, containing mostly Fe, Mn, Zn and Cu (Garcia Ramos, 1979). The presence of organic materials could not be conclusively demonstrated by the spot test analysis (Feigl, 1966). However, it appears that small areas of the painting were finished in tempera, though no correlation has been found between tempera zones and decay. Visible decay is limited to zones close to the window and door, where infiltration leads to a high wall humidity which, together with condensation, is the most important cause of fungal growth. Furthermore, much dirt has accumulated in the rough surfaces of the wall paintings, which have apparently never been cleaned. The very moderate temperature throughout the year in Huelva also contributes to active fungal development.

TABLE 3

Climatic and environmental conditions in Huelva

Season	T (°C)	RH (%)	Total rainfall (mm)	Days 400 $\mu\text{g}/\text{m}^3$ SO_2	Max. SO_2 value
Spring	19.4	60	85	8	954
Summer	24.9	55	18	5	516
Autumn	15.5	69	206	43	6.087
Winter	13.1	72	221	48	2.985

Table 3 shows the mean seasonal values of temperature, relative humidity and mean total rainfall in the period 1961-1979 in Huelva. The table also indicates the number of days with a sulphur dioxide level higher than $400 \mu\text{g}/\text{m}^3$ and maximum 24 hr mean concentration obtained during the period October 1975 - March 1980. Data available from a sulphur dioxide sampling gauge at the monastery, gave mean monthly values for April-August 1980 of 120 (565), 228 (526), 405 (974), 242 (694) and 191 (628) $\mu\text{g}/\text{m}^3$. Figures in brackets indicate the maximum 24 hr mean concentration. In comparison, the U.S. Primary Air Quality Standard for sulphur dioxide is $80 \mu\text{g}/\text{m}^3$ as annual arithmetic mean, and the maximum 24 hr concentration not to be exceeded more than once per year is $365 \mu\text{g}/\text{m}^3$ (Wilson and Jones, 1974).

No data are available for hydrogen sulphide, ammonia and oxides of nitrogen, but it is suspected that the levels are greater than usual because of the proximity of several industrial plants which normally emit these compounds.

Sulphur dioxide has a deleterious effect on frescoes. In fact, this gas is the most harmful air pollutant known for both organic and inorganic materials. It has been reported that $300 \mu\text{g}/\text{m}^3$ of sulphur dioxide can produce about $10 \mu\text{g}/\text{m}^3$ sulphuric acid at 50% relative humidity and twice as much in fog with 100% relative humidity (Winkler, 1976). Contact of sulphur dioxide polluted air with calcareous materials tends to produce a hard crust of gypsum on the exposed surfaces. This development starts with dissolution of cal-

cium carbonate by the strong sulphuric acid formed, and leads to the production of a solution of anhydrous calcium sulphate out of which the dihydrous form, gypsum, is precipitated. The deposition of gypsum under normal circumstances usually results in a colourless or white crystals aggregate (Stambolov, 1967). This agrees with the studied efflorescences described in this article. It is of interest the typical gypsum crystallization (EDAX only showed S and Ca) and fungal contamination were also found in frescoes without evidence of decay (figures 5 and 6).

It is clear that sulphur compounds may influence the microbial ecology of frescoes. Several authors (Pochon and Jatton, 1968; Paleni and Curri, 1972; Tiano et al. 1975) have shown that sulphur-cycle bacteria play a role in stone deterioration. Sulphur oxidising bacteria exceeding 50.000 per gram of sample are regarded as indicatory of biological attack of monuments. Most-probable-number of sulphur oxidising bacteria from efflorescences gave values as great as 65.000 and sulphur reducing bacteria accounted for 200 per gram of sample. These results indicate that these numbers, together with a direct chemical aggression of air pollutants, provide the adequate ecological conditions to promote growth of sulphur-cycle bacteria and, subsequently, to initiate bacterial degradation of the surface of the frescoes. However, the effect of bacteria must be considerably smaller than that produced by air pollution.

The presence of autotrophic chemosynthetic aerobic and anaerobic microorganisms which utilize sulphur as energy source is of the upmost importance because it may represent the first supply of organic matter to frescoes. Death and lysis of such bacteria will promote the growth of other heterotrophic microorganisms. In fact, numerous bacteria with different kinds of metabolism are associated with the sulphur-cycle bacteria, particularly in the efflorescence areas; these include especially ammonifying bacteria (*Micrococcus*, *Bacillus*, *Pseudomonas*) and actinomycetes (*Nocardia*-like and *Streptomyces* species). The most abundant bacterium was *Micrococcus luteus*, which has also been found in decayed frescoes by Tonolo and Giacobini (1963). The role of these bacteria in deterioration of

frescoes was stressed by Lazar (1971) and Lazar and Dumitru (1973).

Fungi may also take part in decomposition of dead bacterial structures or even fungal structures.

Another explanation for the growth of microorganisms on frescoes is the existence of hydrocarbons and volatile organic chemicals in the atmosphere, emitted by the neighbouring oil refineries and cellulose pulp plants. It has been reported that the surface of condensing films tends to entrain and dissolve volatiles. Substances dissolved in water become concentrated as water evaporates, leaving a layer of organic contamination thick enough to provide a substrate for growth of microorganisms. Volatile substances can also react photochemically in the atmosphere, producing aerosols which condense on surfaces (Rasmussen et al., 1968).

In the last sample a mite, *Tyrophagus palmarum* Oudemans, was found feeding of the bacteria and fungi on the frescoes. This mite actively mediates the dispersal of microorganisms attached to the appendages, body surface and cuticular hairs. At the same time, the mite may serve to control the microbial population. The mite requires high temperatures, from 18 to 30°C, with optimum at 23°C, and relative humidity above 85%. In summer, the mean external relative humidity was about 50% while inside the room it was considerably higher, often attaining as much as 90%. The environmental conditions therefore favour the growth of other organisms than only fungi and bacteria.

The study presented here indicates that frescoes are populated by a varied fungal flora together with bacteria and mites. From these results it is clear that a close link exists between the bio-deterioration of the frescoes of the monastery of "Santa Maria de la Rabida" and the environmental pollution, though humidity can be considered a starting point of deterioration.

Some attempts were made by the architect-restorer to eliminate wall humidity, such as construction of a damp course using an epoxy resin, covering of the exterior surfaces with an impermeable layer of rendering, and installation of an air conditioner to ensure stabilization of the relative humidity at 60-70%.

Slow drying of the damp walls is recommended before an air conditioner is used, as well as consolidation of the picture layer, cleaning and biocide treatment. Further gas sterilization might be required in order to complete the elimination of bacteria, fungi and mites. Laboratory tests showed that ethylene oxide and methyl bromide are effective against selected isolates of these organisms. However, as environmental pollution cannot be controlled it is not known how this will effect the frescoes in the future.

Acknowledgements

The authors are grateful to Dr. A. Jimenez and Mr. J.M. Cabeza, architect-restorers, and to Fra. F. Oterino, prior of the monastery, for providing facilities for this research. We wish to acknowledge Centro Meteorologico Zonal, Badajoz, and Junta de Andalucia, Consejeria del Medio Ambiente, Huelva, for supplying data to complement table 3, Mr. F. Bernier for scanning electron microscopy and EDAX analyses, Dr. C. Perez-Iñigo for mite identification, Mr. E. Filgueras for photographic works and Miss D.N. Rodriguez for technical assistance. Dr. C.A.N. van Oorschot kindly corrected the English text.

References

- Bassi, M. and Giacobini, C. (1973). Scanning electron microscopy: A new technique in the study of the microbiology of work of art. *Int. Biodetn. Bull.* 9: 57-68.
- Drescher, R.F. (1958). Microbiology of paint film. IV. Isolation and identification of the microflora on exterior emulsion paints. *Am. Paint J.* 42: 80-102.
- Feigl, F. (1958). Spot test in inorganic analysis. Elsevier Pub. Co. Amsterdam.
- Feigl, F. (1966). Spot test in organic analysis. Elsevier Pub. Co. Amsterdam.
- Garcia Ramos, G. (1979). Estudio fisico-quimico, mineralogico y bio-

- quimico de algunas pinturas y revestimientos murales de La Rabida, Huelva. Unpublished report.
- Gargani, G. (1968). Fungus contamination of Florence artmaster pieces before and after the 1966 disaster. In Biodeterioration of Materials. A.H. Walters and J.J. Elphick, eds. Elsevier Pub. Co. Amsterdam, pp. 252-257.
- Garret, S.D. (1963). Soil fungi and soil fertility. Pergamon Press, Oxford.
- Giacobini, C. and Lacerna, R. (1965). Problemi di microbiologia nel settore degli afreschi. Boll. Ist. Cent. Restauro, 1965: 83-108.
- Groupe Biologie de la Conservation de la Pierre (1976). Rapport No. 372.
- Ionita, I. (1973). Contribution to the study of the biodeterioration of work of art and historic monuments. IV. Fungi involved in the deterioration of mural painting from the monasteries of Moldavia. Rev. Roum. Biol. Botanique, 18: 179-189.
- Lazar, I. (1971). Investigations on the presence and role of bacteria in deteriorated zones of Cozia monastery painting. Rev. Roum. Biol. Botanique, 16: 437-444.
- Lazar, I. and Dumitru, L. (1973). Bacteria and their role in the deterioration of frescoes of the complex of monasteries from northern Moldavia. Rev. Roum. Biol. Botanique, 18: 191-197.
- Mora, P., Mora, L. and Philippot, P. (1977). La conservation des peintures murales. Editrice Compositori, Bologna.
- Paleni, A. and Curri, S. (1972). Biological aggression of works of art in Venice. In Biodeterioration of Materials, vol. 2, A.H. Walters and E.H. Hueck van der Plas, eds. Applied Science Pub., London, pp. 392-400.
- Park, D. (1968). The ecology of terrestrial fungi. In The Fungi, vol. III, G.C. Ainsworth and A.S. Sussman, eds. Academic Press, New York, pp. 5-39.
- Pochon, J. and Jaton, C. (1968). Facteurs biologiques de l'alteration des pierres. In Biodeterioration of Materials. A.H. Walters and J.J. Elphick, eds. Elsevier Pub. Co., Amsterdam, pp. 258-268.
- Rasmussen, R.A., Hutton, R.S. and Garner, R.J. (1968). Factors in

- establishing microbial populations on biologically inert surfaces. In *Biodeterioration of Materials*. A.H. Walters and J.J. Elphick, eds. Elsevier Pub. Co., Amsterdam, pp. 79-98.
- Savulescu, A. and Ionita, I. (1971). Contribution to the study of the biodeterioration of the works of art and historic monuments. I. Species of fungi isolated from frescoes. *Rev. Roum. Biol. Botanique*, 16: 201-206.
- Stambolov, T. (1967). Effect of sulphur pollution on building materials. IIC Conf. on Museum Climatology, London, pp. 15-20.
- Tiano, P. and Gargani, G. (1976). Controlli microbiologici su alcuni affreschi fiorentini. *Atti Convegno a 10 anni dell'Alluvione*, Firenze.
- Tiano, P., Bianchi, R., Gargani, G. and Vanucci, S. (1975). Research on the presence of sulphur-cycle bacteria in the stone of some historical building in Florence. *Plant Soil*, 43: 211-217.
- Tonolo, A. and Giacobini, C. (1963). Microbiological changes of frescoes. In *Recent Advances in Conservation*. G. Thomson, ed. Butterworths, London, pp. 62-64.
- Tresner, H.D. and Hayer, J.A. (1971). Sodium chloride tolerance of terrestrial fungi. *Appl. Microbiol.* 22: 210-213.
- Wilson, R. and Jones, W.J. (1974). *Energy, ecology and the environment*. Academic Press, London.
- Winkler, E.M. (1976). Weathering rates of stones in urban atmospheres. In *The Conservation of Stone*. R. Rossi-Manaresi, ed. Centro per la Conservazione delle Sculture all'Aperto, Bologna, pp. 27-36.

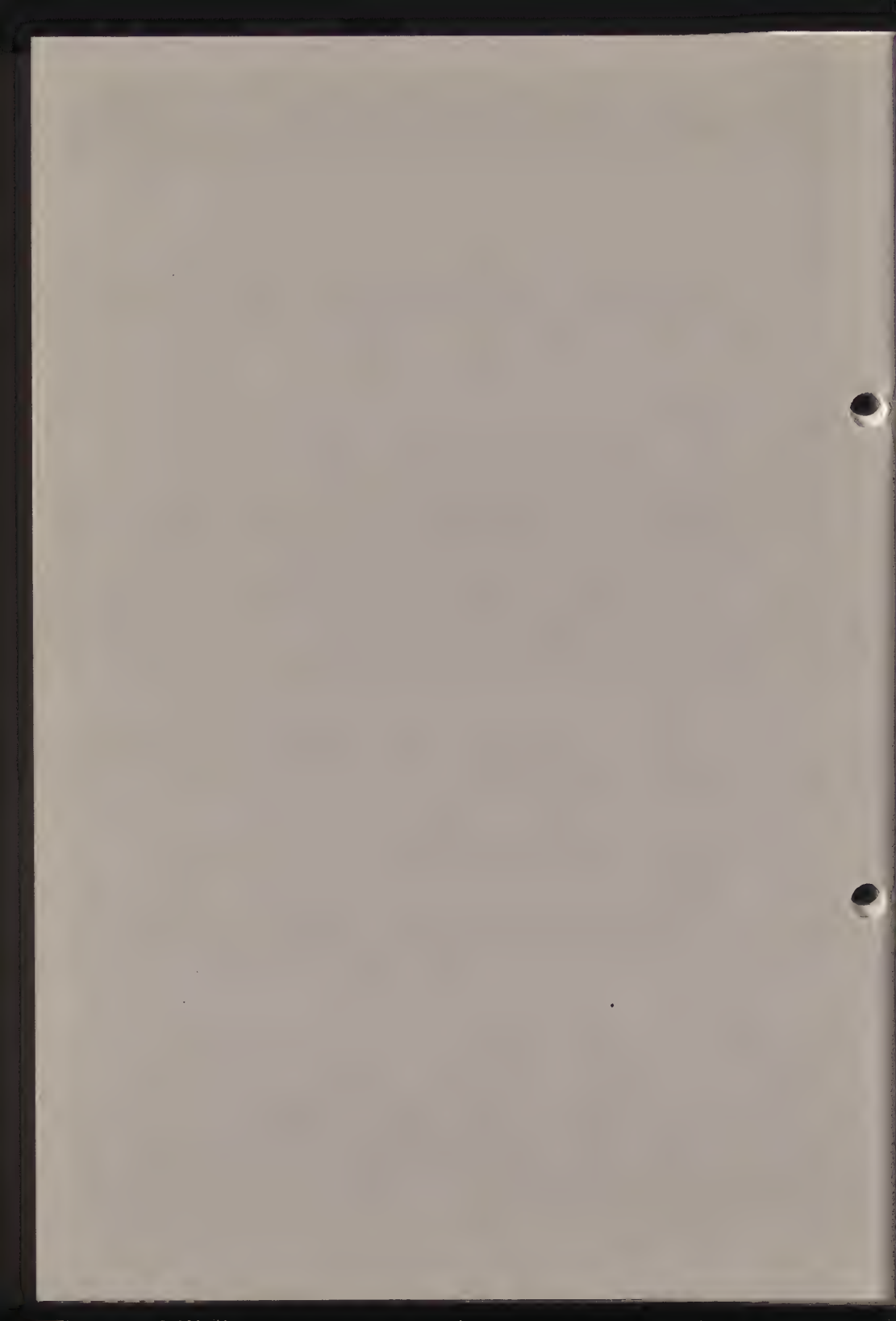
81/15/6

L'ATTRIBUTION DU FRAGMENT DE LA PEINTURE
MURALE DE 1237 A LA CATHEDRALE D'ASSOMPTION
DANS LA VILLE DE VLADIMIR

Victor Filatov

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Peintures murales et
mosaïques



L'ATTRIBUTION DU FRAGMENT DE LA PEINTURE MURALE DE 1237 A
LA CATHEDRALE D'ASSOMPTION DANS LA VILLE DE VLADIMIR

Victor Filatov

Gorodok Baoumana, 3, korp. 4
105037 Moscou
URSS

La vérification de la date de la création d'un fragment de la fresque dans la Cathédrale d'Assomption à la ville de Vladimir sur la base de la comparaison des résultats des analyses pétrographiques des enduits de plâtre, la description des procédés et des styles de la peinture en résultat des travaux de restauration réalisés par une équipe de peintres - restaurateurs de l'Atelier de restauration de Vladimir.

Les matériaux de construction essentiels de l'architecture du Principauté Vladimirskoye des XII-XIII s.s. étaient le calcaire blanc, la pierre sédimenteuse, dont était riche cette région. Les parties principales des remparts de la ville de Vladimir, "Les Portes d'Or," conservée jusqu'aux nos jours, les palais des Princes-térèmes d'Andrei Bogolubski et ceux de la résidence Bogolubov, un grand nombre d'églises et la Grande Cathédrale d'Assomption étaient construits en pierre blanche par Andrei Bogolubski et ses successeurs.

1238 la ville était détruite par les hordes tartares.

L'architecture en pierre blanche diffère de l'architecture d'autres villes, celles comme, par exemple, Kiev, Smolensk, Pskov, Polotsk, Novgorode, où les matériaux de construction étaient non seulement le bois, mais aussi la brique cuite ("plinpha"). Les chaux pour les constructions d'architecture et pour les fresques qui ornaient, comme les fameux reliefs sculptés, des murs des Cathédrales, était préparée aussi en calcaire de la région.

Les analyses petrographiques des enduits des fresques des XII-XIII s.s. ont démontré que le charge minéral essentiel était le calcaire blanc pilé local. Ces analyses étaient faites par les collaborateurs de l'Institut des recherches scientifiques de la ville de Minsk, d'après les échantillons prises par le peintre-restaurateur A.Nekrassov et par le chimiste-restaurateur A.Baliguina.

L'utilisation du charge en calcaire par les maîtres de Vladimir témoigne la succession de la tradition antique en ce qui concerne de l'utilisation du coquillage et du marbre. Cela se distingue de l'utilisation des débris céramiques et du sable aux enduits dans les constructions architecturales d'autres Principautés de cette époque-là.

Au cours des travaux de restauration réalisés les dernières années à la Cathédrale d'Assomption

les dernières années à la Cathédrale d'Assomption dans la ville de Vladimir, on a réalisé les analyses petrographiques des enduits aux fins de l'argumentation technologique de l'époque de la création des fresques de la Cathédrale. Sur la base de ces données et celles des croniques où se sont mentionnées des travaux de réparage et de reconstruction, on avait établi l'existence des étapes suivantes:

II6I - la fin des travaux de construction et la décoration de fresques de la Cathédrale

II89 - l'agrandissement de la Cathédrale après l'incendie de II85, sa reconstruction et la création de nouvelles fresques

I237 - la peinture des nartex construits en II89

I408 - la repeinte des fresques dans tout la Cathédrale, au moitié du XVII siècle la repeinte suivante de la peinture murale.

I769-I774 - la repeinte des fresques

I882 - la dernière grosse repeinte des fresques et la création de nouvelles.

I9I8-I925 - la découverte de la majorité de fragments des peintures murales des XII, XV, XVII s.s.

I932, I946, I968 - les travaux de conservation des fresques.

Au cours de tous les travaux de renouvellement et de repeinte, jusqu'aux travaux de I882, on det-

ruisait les fragments vétustés et on "complétait" la peinture. Depuis 1882, on a commencé des recherches et des découvertes de couches antérieures, des fragments conservés. Les dernières années, les peintres-restaurateurs de l'Atelier de Vladimír ont découvert encore quelques uns, avant ignorés, des fragments des XII et XV siècles. Pour l'attribution des fragments découverts récemment et la vérification des fragments découverts avant, on a réalisé une série de recherches. Sur les résultats des recherches réalisées et la restauration des peintures murales de I408 à la Cathédrale d'Assomption, à cette Conférence sera présenté le rapport de L.Baliguina et A.Nekrassov. Mon rapport est consacré à l'attribution ne qu'un fragment, découvert en 1918-1925 à la mur de Sud de la Cathédrale. La fresque est dégagée sous la direction de l'académicien I.Grabar et, premièrement, elle était définit comme l'oeuvre de I408. Depuis les années cinquantes on a commencé de l'attribuer à I237. Quand on procédait ces attributions, la peinture était couverte d'une couche épaisse de suie et de poussière. C'est probablement pourquoi, les particularités de la peinture, l'analyse stylistique n'a été jamais fait. On se limitait de la mentionner par quelques mots, en la rapportant à la composition "Miracle de Théodor Thiron".

Il faut noter, que le contour de l'ovale du visage conservé ne garde aucune allusion à la barbe, attribut nécessaire iconographique de Théodor Thiron. Selon toute probabilité que sur cette mur, construite en 1189, affectée aux tombeaux des Princes de Vladimir, étaient représentées les miracles opérées par Guéorgui le Vainqueur. Il était le Saint protecteur du prince Youri Dolgorouki, grand-père de Guéorgui Vsevolodovitch II et du prince Guéorgui II, à l'époque duquel pourrait être faite cette fresque. Une telle icône du jeune Guerrier est propre à Dimitri, en l'honneur duquel le prince Guéorgui II a érigé la cathédrale près de la grande Cathédrale d'Assomption, où se trouvait le fragment dont nous nous intéressons.

Le fragment conserve n'est pas grand. On n'y voit que la figure du jeune guerrier, en mouvement dynamique de l'Est à l'Ouest(c'est-à-dire dans le sens inversé que les autels). Sa tête est entourée de nimbe et tournée à trois quart, un peu penchée en avant. Ses épaules sont ouvertes presque en face. Son torse et ses hanches sont penchés en avant. On pourrait dire que son bras est soulevé pour le coup d'épée. Son bras gauche est baissé et un peu plié en coude. Le guerrier s'appuie à la jambe gauche, plié au genou et poussée en avant. Il s'écarte à

à l'aide de sa jambe droite pour renforcer le mouvement de son corps en avant. Le Saint guerrier (ce que confirme son nimbe), se moivoie sur le fond de la montagne d'un jaune vif. Le fond est bleu, dont se conservait la couche de préparation d'une grise pâle. Le guerrier est vêtu d'une cuirasse(l'ocre jaune vif) à la bandoulière à travers l'épaule gauche. Sa chemise est grise pâle aux ombres rouges-brunes. Les pantalons sont roses-grises aux lignes rouges-marrons des contours et des ombres. Ses bottes sont blanches aux bandeaux jaunes.

Au cours des recherches petrographique des enduits des premières fresques de la Cathédrale d'Assomption on a déterminé que le charge essentiel des mortiers de chaux était les debris de calcaire, et on a reussi d'établir la différence des enduits des époques différentes(XII-XIII s.s.). On y peut s'assurer en faisant la comparaison des résultats des analyses du fragment dont nous nous intéressons et les enduits des pylones construites en 1189, où se sont représentés les prophètes.

La mur du ^a nrtex de Sud
(l'image du guerrier)

Dans la lame mince transparente

Le liant - 50%

Le charge - 40%

Les pores - 10%

Le pylône gauche d'Est
(l'image des prophetes)

Dans la lame mince transparente

Le liant - 20%

Le charge - 70%

Les pores - 10%

Le liant

La masse de chaux, cristallisée irrégulièrement, en général d'une fine dispersion, la présence de la pâte de chaux.

Le charge

- Le calcaire, la dimension des débris est de 0,15 aux 2-3 mm. D'après les grands débris on peut voir que le calcaire est poreux, aux granules fines et sa structure se distingue peu de celle du liant. De petits débris ont les contours nets, aux petites granules, épais. Les granules de quartz sont peu nombreuses les dimensions ne surpassent pas 0,3 cm., elles sont probablement, l'addition naturelle aux matières première, il y a peu de charge fibreux: les fibres minces ont l'épaisseur 0,01 mm, la longueur 0,4 mm, elles sont mises en faisceaux. La présence des pores droites dans

Le liant

La masse de carbonat de calcium, submicroscopique, homogène.

Le charge

Le principale des débris de calcaire à fine dispersion. De petits débris sont de la structure épaisse, les grands la matière poreuse. Les granules de quartz sont peu nombreuses, à 1%, la dimension à peu près de 0,1 mm. Probablement, elles sont l'addition naturelle. Les débris céramiques sont peu nombreux, ne surpassent 0,2 mm de diamètre. L'alumine est avec l'addition de quartz (0,02 mm, aux petites granules)

les lames minces (largeur 0,5, longueur 10 mm) témoigne l'introduction de la paille dans le mortier.

Les pores

- comme la règle, elles sont isométriques aux contours irréguliers, de dimension prédominante 0,01-0,5 mm.

On voit les débris de charbon, le charge fibreux à 1%, les fibres sont fines 0,1-0,3 mm, mises en faisceaux.

Les pores

- d'une forme ronde force de porosité du charge, les craquelures de 0,01 mm. sont peu nombreuses.

La composition et la structure des enduits sont différentes, et, par conséquent, les fresques sont peintes par de différentes équipes de maîtres, mais dans la même tradition "vladimirienne".

Les procédés de la peinture sont aussi bien différentes. Le premier dessin du guerrier est fait avec l'ocre jaune, fortement dilué de l'eau-. Le nombre est griffé sur le plâtre cru, de l'épaule à l'épaule. Les surfaces du nimbre et des cuirasses sont couvertes d'ocre jaune. Avec la couleur grises liquide le peintre a fait le contour du torse, de la tête, du visage, la bandoulière. Avec la même couleur il a coloré le fond. Avec l'ocre jaune vif est faite la couche de préparation de la montagne et cette couleur a dépassé le contour des jambes. La couche épaisse de préparation

pour la chemise, le peintre a mis avec la couleur grise (le mélange de la couleur noir avec les blancs de chaux). Avec l'ocre jaune additionné de blanc de chaux, le nimbe est peint pour la deuxième fois. Les cuirasses sont faites avec la même couleur, parfois par la couche lisse, parfois par le dessin graphique. D'une manière particulière sont particulières sont peints les réhauts sur la chemise grise. En général, on faisait les réhauts par intermédiaire de l'application des couleurs plus en plus claires, grâce à l'addition des blancs à la couleur principale. A cette fresque le peintre a utilisé les qualités lisses des blancs, mis par une couche fine. Ce procédé témoigne le maniement virtuose du peintre des particularités des couleurs différentes. La tête du guerrier est peinte non sur la couche de préparation jaune du nimbe, mais sur la couche verdâtre, laquelle a décidé l'image du visage, du cou, des cheveux. Sur cette couche de préparation verdâtre sont dessinés les traits du visage, des cheveux, mais avec la couleur liquide marron. Les endroits clairs du visage sont faits par l'intermédiaire de l'intensification de l'ocre jaune dilué par les blancs de chaux (la carnation). Malheureusement, l'image du visage est presque perdue.

De haute qualités artistiques, la maîtrise brillante, la connaissance des particularités techno-

logiques du palitre restreint des fresques, la liberté de la représentation du mouvement dynamique de la figure, tout cela témoigne l'art perfectionnée de l'équipe de peintres locaux qui ont peint les pylônes et d'autres parties de la Cathédrale d'Assomption construites à l'époque du prince Vsevolode en 1189.

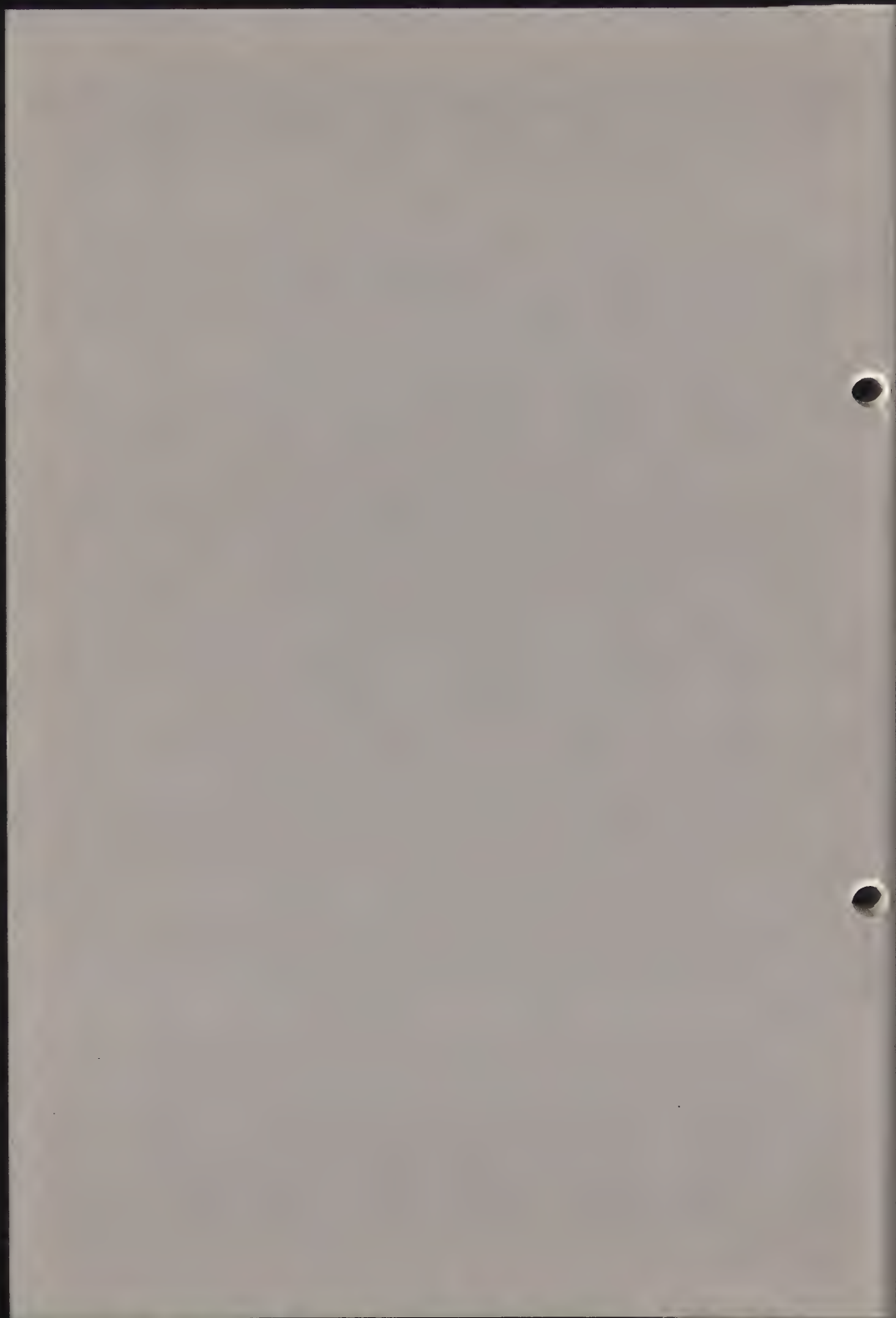
La situation du fragment conservé à la mur de Sud de la Cathédrale, la grande maîtrise de sa réalisation, la différence de la composition de l'endroit de la peinture murale de 1189, donnent la possibilité d'attribuer ce fragment à 1237.

LES RESULTATS DES RECHERCHES ET DE LA
RESTAURATION DES PEINTURES MURALES A LA
CATHEDRALE D'ASSOMPTION DANS LA VILLE DE
VLADIMIR EN 1408

Ludmila Baliguina et Alexandre Nekrassov

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Peintures murales et
mosaïques



LES RESULTATS DES RECHERCHES ET DE LA RESTAURATION DES
PEINTURES MURALES A LA CATHEDRALE D'ASSOMPTION DANS LA
VILLE DE VLADIMIR EN 1408

Ludmila Baliquina et Alexandre Nekrassov

Rue Nekrassov 6
600000 Vladimir

Les resultats des recherches par l'intermediaire des rayons ultraviolets filtrées et en lumière diurne des fresques de 1408 , faites par les peintres Andrei Roublev et Daniil Tcherni à la Cathédrale d'Assomption dans la ville de Vladimir; les donnés des analyses chimiques et phisico-chimiques des matériaux de la peinture. Le bilain des travaux de restauration et de la conservation. La vérification des attributions historico-artistiques sur la base des resultats des recherches réalisées.

La fresque unique d'Andrei Roublev et de Daniil Tcherni de 1408 à la Cathédrale d'Assomption de XII s. dans la ville de Vladimir au cours de 500 années était quelques fois renouvelée et repeinte. On a commencé le dégagement des fresques des couches ultérieures depuis la II-ème moitié du XIX siècle et leurs étude orientée- depuis le 1918, juste après la Grande Révolution d'Octobre en Russie.

En 1969 l'Atelier de la restauration scientifique et de production de Vladimir a décidé de réaliser à la Cathédrale d'Assomption les travaux de recherches scientifiques aux fins de l'identification des procédés et des matériaux pour la restauration des peintures murales faites par Andrei Roublev et Daniil Tcherni en 1408, des peintures fort endommagées. Le candidat en histoire de l'art, V. Filatov, l'ingénieur A. Ivanova, chimiste, dirigeaient ces travaux. Etaient commencé le travail orienté et systématique sur l'examen de la technologie et les matériaux des peintures anciennes, leurs état et leur conservation. Il faut noter que les études des fresques d'Andrei Roublev avait été réalisé plus tôt. C'étaient l'académicien I. Grabar, professeur N. Saritchev, V. Lazarev, M. Alpatov et d'autres historiens d'art et des restaurateurs qui travaillaient à la Cathédrale aux époques différentes. Mais tous ces travaux on peut référer aux études historico-artistiques. Nous avons eu pour le but l'étude des fresques au point de vue de la science et de la technique. On a réalisé l'étude détaillée des fresques dans la lumière du jour et en ultraviolet, les recherches phisiques et phisico-chimiques des matériaux de la peinture datant 1408, c'est-a-dire des couleurs et de la couche d'enduit. On n'a pas réalisé des recherches du liant des fresques, parce que d'après les documents d'archives il était constaté que de 1929 à 1965, la peinture avait été renforcée quelques fois par la colle de caséine.

I. L'étude de la peinture dans les rayons ultraviolets

L'étude des fresques dans les rayons ultraviolets était réalisée par les spécialistes de l'Institut "Spetsproyektrestavratsia", photographe E.Fedorov sous la direction de l'historien d'art V.Filatov. L'étude réalisée a révélé les dessins et les couches récents, la couche originelle de couleur, les inscriptions mal lisibles et les matériaux des restaurations précédentes. Par exemple, la luminiscence en ultraviolet filtré de la peinture de la grande voûte en anse de panier, a produit les contrastes et a découvert les additions tardives en plâtre et alabastré dans la grande quantité de trous d'injection. Telle quantité de trous d'injection prouve, évidemment, dit sur quelques étapes du renforcement par le plâtre des enduits des fresques. D'ici est compréhensible l'origine des efflorescences de sulfate, situées sur la surface de la couche colorée.

Les couleurs authentiques de Roublev sont devenues très contrastes, les inscriptions ne donnaient pas du contraste. Dans les cas de la perte de la couche colorées des visages des apôtres, en rayons ultraviolets on a vu distinctivement les traits originaux.

A la retombée de Sud, à la composition "Terre et l'eau rendent les morts", se sont révélées les traces des inscriptions en blancs, invisibles à la lumière du jour.

On a réussi de lire l'inscription droite "La mer rend les morts".

A la voûte petite en anse de panier, sous les choeurs, est decouvert un grand nombre d'efflorescences luminiscentes, de trous d'injection, d'additions en plâtres et de gerçures.

Le resultat de l'étude de la peinture sur les parties supérieures des images des Vénérables Antoni le Grand et d'Onoufri situées à l'arc d'Est de la voûte de Sud, a surpassé tout attente. A côté de Nord de l'arc, l'image d'Antoni le Grand s'est bien conservée et sa tête ressemble à celles d'autres, peintes en 1408 par Andrei Roublev et Daniil Tcherni. Mais à la pente de Sud, sur la représentation de la tête du Vénérable Onoufri, passée pour bien conservée, depuis 1408, on a decouvert d'importantes couches ultérieures, les efflorescences et les trous d'injection. Il est etabli que de l'image de 1408 n'a resté que le contour et une partie de carnation. Tous les traits du visage et les cheveux sont peints, probablement, au sciecle précédent.

Encore un fait attire l'attention. A la composition "Présentation de la Vierge au Temple", dans le groupe de jeunes filles, encore une fille en voile est apparue. Son bras droit est plié. En lumière du jour on ne voit pas cette image.

A la même composition se sont conservés deux

textes ayant les contrastes différentes dans les petites est faible, les caractères plus grandes produisent la lueur trouble jaune. Probablement, dans la couleur de la couche supérieure il y a l'addition des blancs de plomb. L'analyse chimique a confirmé cette supposition.

II. L'étude des matériaux des fresques de I408 d'Andrei Roublev et de Daniil Tchernii

Pour l'exécution de l'étude des matériaux de la peinture on a fait les analyses suivantes.

- 1). L'analyse qualitative chimique des couleurs des fresques
- 2) L'analyse radiographique structurelle des pigments bleus et verts
- 3) Les analyses petrographique et chimique qualitative des enduits de plâtre.
- 4) La définition de l'absorption d'eau et de la porosité des enduits des fresques de I408

L'analyse chimique et radiographique structurelle des couleurs des fresques de Roublev ont montré la présence des pigments suivants: l'ocre jaune, l'ocre rouge, le vermillon de mercure, l'outremer naturel, la terre verte, la terre brûlée de Sienne, les blancs de plâtre, le carbonate noir. Tous les couleurs intermédiaires sont obtenues grâce au mélange de ces pigments.

On peut noter que ces peintres n'utilisaient pas du vermillon de mercure pur, toutes les couleurs rouges

sont le résultat du mélange de l'ocre avec le vermillon de mercure ou sont l'ocre rouge.

L'analyse chimique des enduits des fresques d'Andrei Roublev a montré que l'enduit contient 94% du liant de carbonat en chaux magnésienne et 5,3% résidu insoluble, où on a trouvé les granules de quartz et les fibres de chanvre. Ici on peut noter, que au cours de l'analyse, il est possible le transfert dans le mortier non seulement du liant, mais aussi d'une partie de charge de carbonat, utilisé très souvent en Russie dans les enduits de plâtre des monuments. C'est exactement pour cette raison, qu'on a réalisé une série d'analyses petrographiques pour préciser la composition des enduits des fresques de I408. L'examen visuel et l'observation des lames minces transparentes au microscope au diapason d'augmentation 70+160 ont permis d'établir, que toutes les échantillons des enduits représentent les mortiers de plâtre avec une petite addition de charge de carbonat, fibreux et des grains de sable, en general, du quartz. La masse du carbonat de calcium aux fins cristaux, en qualité de liant, constitue de 85 à 96 % de la matière. Dans toutes les échantillons il y a des additions de carbonate ayant la structure aux plus grands cristaux que celle de la masse essentielle. La dimension des granules formants ces additions est à peu près 0,01 mm, la dimension des additions elles-mêmes varie

de 0,03 à 0,3 mm, plus rarement jusqu'au 0,1 mm. Ces

additions ont la forme ronde ou irrégulière. Les additions plus importantes contiennent, en général, une grande quantité de pores de la forme irrégulière; parfois ces pores occupent plus de la moitié de volume d'additions.

La quantité de charge fibreuse est petite dans les échantillons isolés, et plus grande dans les autres. Cela se peut expliquer par le remuage irrégulier pendant la préparation du mortier; on trouve très rarement les granules de quartz de 0,2 mm. Les enduits des fresques de Roublev sont, en général, carbonisés régulièrement et seulement dans quelques lames minces à fine dispersion CaCO_3 à une certaine hétérogénéité. Cela s'explique, avant tout, par la hétérogénéité de la pâte originale de plâtre, par rapport avec quoi cette masse se carbonisait irrégulièrement. Outre cela on a fait la définition de l'absorption d'eau et de la porosité des échantillons des enduits de plâtre des fresques de Roublev. Les analyses ont démontré: l'absorptivité d'eau de l'enduit est 37%, la porosité-14,1%.

Pour faire comparer la composition des enduits de plâtre, on a réalisé les analyses des matériaux de fresques de 1408, 1161, 1237 et de la moitié du XVII s. sur les murs de la Cathédrale. Les enduits des fresques de 1408 se distinguent d'une manière évidente de ceux d'autres d'après leur composition. Ainsi, sur la base

des recherches exécutées, les fresques attribuées à Roublev, ~~appartiennent~~ vraiment à ce maître. De ce fait, il convient introduire quelques corrections aux attributions faites avant ce jour-là. Par exemple, l'academicien I. Grabar, dans son article "Andrei Roublev" écrit: "... à la mur de Sud de la Cathedrale de Vsevolode est decouverte... encore une fresque, se rapportant à l'epoque de Roublev, elle represente un guerrier-martyre inconnu". Mais, V. Lazarev, et ~~p~~ares lui d'autres savants ont attribué ce fragment aux vestiges des peintures murales de 1237.

Nos recherches des matériaux de la peinture de ce fragment ont confirme la supposition de V. Lazarev, c'est - à- dire, le fragment decouvert par I. Grabar, n'est pas la peinture de Roublev, mais elle date le 1237. En ce qui concerne les peintures sur les pylônes deriere l'iconostase, attribuées par N. Sitchev au XII siècle, il n'y a aucune doute quelles appartiennent à 1408. Les croix du Calvaire, peintes au-dessous sont de 1161. Outre cela, on refute la supposition de N-Sitchev sur l'attribution de la composition "La présentation de la Vièrge" au Temple" et "Le refus des dons de Yokhime et d'Anne". Il a supposé que "... l'original était fait en XII s. et repeint par Roublev en 1408..." Après le dégagement des peintures récentes, faites en XIX-XX s.s. et d'une couche abondante des encrassements, ~~en~~ en resultat de l'étude des matériaux de la peinture

(des couleurs et des enduits), du style et des procédés, il est décidé d'attribuer ces compositions à I408. Outre cela, en examinant les couleurs des inscriptions sur la Composition de "la Vierge au Temple", il est apparu, que les blancs des lettres des textes en haut, contiennent sauf les blancs de plâtre, mais aussi les blancs de plombe; Le pigment bleu du fond sous ces textes se compose d'azurite, contenant le cuivre analogique à la couleur bleue utilisée au moitié du XVIII siècle; Les mêmes couleurs nous avons trouvé à la composition "La Transfiguration" faite par Andrei Roublev en I408 à la lunette de Nord de la Cathédrale.

A présent, à la Cathédrale d'Assomption est achevée la restauration des peintures murales aux surfaces à peu près de 200 m². Les travaux sur les voutes sous les chœurs et dans l'autel ne sont pas encore terminés.



81/15/8

PERFECTIONNEMENT DE LA METHODE DU TRAITEMENT
DE PEINTURES MURALES SUR UN SUPPORT DE LOESS
AVEC EMPLOI DE POLYBUTYLMETHACRYLATE (FIXATION
PRIMAIRE DE LA COUCHE PICTURALE)

M.P.Vinokourova et E.P.Melnikova

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Peintures murales et
mosaïques



PERFECTIONNEMENT DE LA METHODE DU TRAITEMENT DE PEINTURES
MURALES SUR UN SUPPORT DE LOESS AVEC EMPLOI DE
POLYBUTYLMETHACRYLATE (FIXATION PRIMAIRE DE LA COUCHE
PICTORALE

M.P.Vinokourova et E.P.Melnikova

Musée de l'Ermitage d'Etat
191065 Leningrad
URSS

Résumé

Il s'agit dans l'exposé de l'élaboration de la méthode de fixation de la couche picturale de la peinture murale sur le plâtre de loess, découverte au cours de fouilles archéologiques dans le système du traitement de la peinture murale suivant la méthode d'emploi du polybutylméthacrylate à basse viscosité (PBMA-BV) en tant que fixateur essentiel.

Il a fallu trouver un polymère, répondant à toutes les exigences de restauration, avec les qualités propres au fixateur et n'ayant pas de solvant commun avec l'agent fixatif essentiel - PBMA.

Les collaborateurs de NPO "Plastpolymère" après des recherches dans ce domaine ont proposé le polymère C-8 qui a une masse moléculaire élevée et contenant dans la macromolécule des groupes d'acétal et d'hydroxyle se dissolvant dans le mélange d'alcool.

éthylrique et d'eau.

Du fait des épreuves méthodiques comprenant toutes les étapes du traitement in situ et au laboratoire on a établi que le double enduit de la couche picturale avec la solution du polymère C-8 de 2% dans le mélange des solvants - alcool éthylique/eau (70:30) forme sur la surface une pellicule poreuse, élimine l'état poudreux de la couche picturale, permet aux solutions du fixateur essentiel - PBMA-BV de pénétrer sans difficultés à l'intérieur du plâtre et réaliser les étapes ultérieures du traitement des peintures murales.

En 1978 le Laboratoire de restauration des peintures murales de L'Ermitage d'Etat a introduit la pratique de la fixation de la couche picturale in situ.

Le problème de conservation des peintures murales sur un plâtre de loess trouvées dans les fouilles des villes moyenâgeuses de l'Asie Centrale a été résolu dans les années 40 à L'Ermitage suivant la méthode qui a pour base l'utilisation du polybutylméthacrylate (PBMA-BV) en tant que fixateur essentiel.

L'élaboration du procédé de fixation préalable de la couche picturale se poursuivait dans le système de cette méthode comme l'une des orientations de cette dernière dans le but de perfectionnement du procédé par le Laboratoire de restauration de la peinture murale en collaboration avec le Laboratoire de chimie de L'Ermitage d'Etat.

En étudiant ce problème posé par le créateur de cette méthode P.I. Kostrov, nous n'avons pas eu la possibilité de s'appuyer sur une expérience d'autrui car nous n'avons pas rencontré dans la littérature lue de méthodes pareilles déjà élaborées.

La couche picturale des peintures murales sur plâtre de loess est pratiquement dépourvue de liant; elle se trouve souvent dans un état poudreux et en séchant, à condition qu'elle ne soit pas consolidée, commence à tomber en poudre.

Très souvent la couche de fond manque et même si elle s'est conservée, elle est friable et mamelonnée et fréquemment se détache du plâtre aussi friable et peu solide. C'est pour cette raison que la couverture de la couche picturale d'une solution fixant la surface de la peinture, surtout la première, couverture est très dangereuse. La solution doit être appliquée avec beaucoup de précautions à l'aide d'un pinceau à poil doux à mesure d'absorption; il ne faut pas admettre de traînées du consolidant car il peut entraîner la couleur et un faux mouvement du pinceau peut déplacer les pigments (par exemple la suie, l'os carbonisé ou le bleu d'outremer). La crasse peut être enlevée avec

le pinceau, pénétrer dans le récipient avec la solution et comme suite avec le consolidant encrassé recouvrir la peinture ce qui complique le nettoyage ultérieur au laboratoire.

On est revenu au problème de protection de la couche picturale consolidée dans les années 70. Il a fallu choisir un polymère ayant les qualités d'un fixatif et répondant à toutes les exigences de restauration. Le fixateur enduit en quantité minimum doit rapidement sécher, arrêter l'état poudreux, ne pas changer la couleur, laisser pénétrer le fixateur essentiel - PBMA -BV à l'intérieur du plâtre pour le consolider et ne pas empêcher le traitement ultérieur des peintures murales. Pour résoudre ce problème on a choisi un polymère qui n'avait pas de solvants communs avec PBMA-BV et qui formait une fine pellicule poreuse sur la surface. C'est pour ces causes-là que l'on a cherché parmi les polymères ayant une masse moléculaire élevée. Au cours des expérimentations au laboratoire on s'est arrêté sur un seul polymère proposé par les collaborateurs de NPO "Plast-polymère" - le copolymère "C-8" contenant dans le macromolécule des groupes d'acétal et d'hydroxyle se dissolvant dans le mélange - alcool éthylique - eau dans les proportions 70:30 et 80:20. Les épreuves des propriétés de la pellicule du polymère "C-8" dans les conditions de vieillissement artificiel au laboratoire de chimie de l'Ermitage (240 heures de vieillissement par la lumière - lampe IPII - 250 à la t° de 30°C et à la distance de 30 cm; 1000 heures de vieillissement thermique à la t° de 60°C) ont montré que la solubilité et la couleur ne changent pas. Ce polymère en qualité de fixatif a été éprouvé méthodiquement et a subi plusieurs étapes.

I-e étape - vérification au laboratoire. Le problème de cette étape - c'est le choix d'une concentration minimum de la solution du fixatif et le minimum de quantité de couverture pour la consolidation de la surface picturale. On a éprouvé les solutions de 1,5%, de 2%, de 2,5%, de 3% et de 4% de concentration dans le mélange du méthyléthylcétone - alcool éthylique - eau dans la proportion de 60:20:20.

On a établi que pour fixer la couche picturale il suffit d'enduire deux fois la surface avec la solution de 2% du mélange alcool - eau dans la proportion de 65:35 ou de 70:30 et dans le mélange méthyléthylcétone - alcool - eau dans la proportion de 60:20:20. Pour fixer les grandes parcelles de préparation se détachant avec la couche picturale il suffit d'une seule couverture avec la solution de 3% du polymère dans ces mêmes mélanges.

La solution du fixatif essentiel (solution du PBMA-BV dans du xylol de 17-20 %) s'imprègne dans le plâtre à travers la surface de la couche picturale consolidée

par la solution "C-8" de 2%.

Les épreuves ont été effectuées sur des échantillons de plâtre authentique - soumis à la cuisson ou non - avec la couche picturale conservée (bleu-outremer, noir-charbon, rose-ocre, rouge).

On rapprochait les conditions de travail autant que possible à celles de in situ: les échantillons ont été humidifiés, reheuffés jusqu'à 26-45°, fixés devant un ventilateur (de table) et un réflecteur. Tous les échantillons traités avaient été soumis au vieillissement dans le régime suivant: un cycle durant 24 heures y compris le chauffage dans un thermostat à la t° de 60°, refroidissement jusqu'à la température ambiante et la mise dans un exsiccateur: en tout 1406 heures dans le thermostat et 7025 heures dans une chambre d'humidification.

L'examen des échantillons au microscope a montré que tous les endroits fixés avec la solution "C-8" de 2% et ceux qui ne l'étaient pas sont dans le même état.

2-me étape - épreuve in situ. Dans les conditions climatiques de l'Asie Centrale il était nécessaire de vérifier les différentes variantes de l'application du fixatif "C-8" aux murs des bâtiments découverts lors des fouilles, couverts de peinture, de vérifier l'état de consolidation du plâtre - du support de la peinture - en procédant à la fixation et ainsi avoir des matériaux pour continuer le travail, car il était à établir si la fixation n'empêcherait pas le nettoyage de la couche picturale salie. On a commencé le travail in situ par des surpeints artificiels. Dans un des bâtiments découvert on a choisi une partie du mur avec le plâtre à la surface lustrée, qui avait la dimension de 2m². On a appliqué sur cette surface des pigments (ocre dorée, blanc, outremer) mélangés avec de l'eau en raies horizontales larges de 10cm sur la préparation blanche et du cadmium rouge, du brun de Mars sur le plâtre.

Toute la surface a été divisée en 10 parties en direction horizontale et verticale. Deux parties pour les soumettre au contrôle: l'une pour vérifier la couleur, l'autre - sans fixation pour comparer la rapidité de l'absorption de la solution PBMA_BV par le plâtre. Les autres parties ont été fixées avec la solution "C-8" de 2% dans différents mélanges de solvants: eau - alcool (30:70), méthyléthylcétone - alcool - eau (60:20:20).

Le fixatif a été appliqué suivant deux moyens: avec un pulvérisateur et avec un pinceau. Chaque variante a été doublée. Le travail se poursuivait ainsi: on appliquait le fixatif suivant l'un des procédés indiqués sur la surface du surpeint. Après l'évaporation du solvant on comparait la couleur à la partie contrôlée. La couleur de la partie fixée n'avait pas changée, les

pigments n'étaient plus à l'état poudreux. Deux heures après on a commencé à consolider les huit parties fixées et la partie qui ne l'était pas avec la solution de 17% de PBMA-BV dans du xylol^{x)} La comparaison a prouvé que la rapidité de l'absorption était la même dans les parties fixées et non-fixées. Immédiatement après la fixation toute la surface imprégnée était étroitement et soigneusement recouverte d'une pellicule de polyéthylène pour 24 heures dans le but de ralentir la vaporisation du xylol. 24 heures après la pellicule a été enlevée et le surpeint a été séché à l'air libre durant cinq jours.

De même dans les conditions in situ la vérification de la possibilité de pénétration du fixatif essentiel dans la couche du plâtre à travers la fixation avec des solutions de concentration élevée a 3-4% a été effectuée. Dans ce cas la pénétration de la solution PBMA-BV à 17% dans du xylol s'est trouvée un peu réduite.

Les épreuves faites sur les surpeints ont affirmé et précisé les données, reçues au laboratoire:

1. La solution "C-8" de 2% dans le mélange alcool éthylique - eau (70:30) après la double application sur la surface de la couche picturale à l'état poudreux après l'évaporation du solvant forme une fine pellicule poreuse superficielle, supprime l'état poudreux et ne modifie pas la couleur de la peinture.

2. La solution du fixatif essentiel - solution de PBMA-BV dans du xylol de 17% pénètre sans difficultés à travers la surface fixée.

3. En qualité de solvant pour le polymère - fixatif a été utilisé le simple mélange d'alcool éthylique - eau en proportion de 70:30.

4. On a vérifié l'utilisation du pulvérisateur pour la couverture de la surface avec la solution d'un fixatif; on a constaté les avantages et l'efficacité de ce procédé.

On a attaché une importance particulière aux expériences faits sur la peinture. Trois fragments ont été choisis à cette intention. Un des fragments après la fixation a été consolidé avec la solution de PBMA-BV dans de l'acétone de 6% (6 couvertures) et a été enlevé en couche mince, les deux autres, comme d'habitude, ont été fixés avec la solution de PBMA-BV dans du xylol et ont été enlevés avec une couche de plâtre. Ces fragments étaient destinés à l'étape suivante de l'expérience qui avait pour but le nettoyage de la couche picturale fixée avec "C-8" et consolidée avec PBMA-BV.

3-me étape - traitement au laboratoire. Chaque échantillon de plâtre avec des surpeints a été divisé en deux parties; l'une d'elles a été destinée au traitement.

x) 15 couvertures

Les huit parties avec différents procédés de fixation avec la solution "C-8" de 2% et une seule sans fixation ont passé toutes les étapes de traitement au laboratoire: 1) Imprégnation supplémentaire avec la solution de PBMA-BV dans du xylol de 10% à l'endroit (6-10 couvertures); 2) Élimination des sels au moyen de trempage et ensuite un séchage ralenti au filtre de papier; 3) Traitement définitif de la surface avec des compresses avec le mélange de méthyléthylcétone - alcool - eau (60:20:20). Le traitement des échantillons à surface fixée s'est effectuée sans complications.

On a accordé une attention toute particulière aux fragments de peinture éprouvés. C'est sur ces fragments qu'on a pu vérifier la possibilité du nettoyage de la surface fixée et consolidée à différentes étapes de traitement.

Le fragment NI - le nettoyage a été effectué après le traitement définitif (élimination de sels, séchage, imprégnation supplémentaire, séchage, enlèvement des surplus de polymère de la surface). Le fragment N 2 - a été nettoyé après le traitement in situ et après avoir enlevé la couche protectrice de gaze. Le fragment N 3 - à couches minces, fixé in situ avec la solution de PBMA-BV dans de l'acétone, nettoyé après le traitement in situ.

Le nettoyage des fragments éprouvés a été effectué suivant deux procédés. Le premier - en utilisant des solvants. La crasse a été amollie en la recouvrant de méthyléthylcétone avec un pinceau et était enlevée avec un scalpel. Si la surface était foncée on la clarifiait avec des compresses imbibées d'un mélange de solvants. Le deuxième - la surface a été traitée en appliquant des compresses imbibées d'un mélange de solvants: méthyléthylcétone - alcool éthylique - eau en proportion de 60:20:20, séchée, ensuite la crasse enlevée avec un scalpel en humidifiant la surface d'eau.

Le traitement au laboratoire a prouvé que la fixation n'empêche pas le nettoyage de la couche picturale.

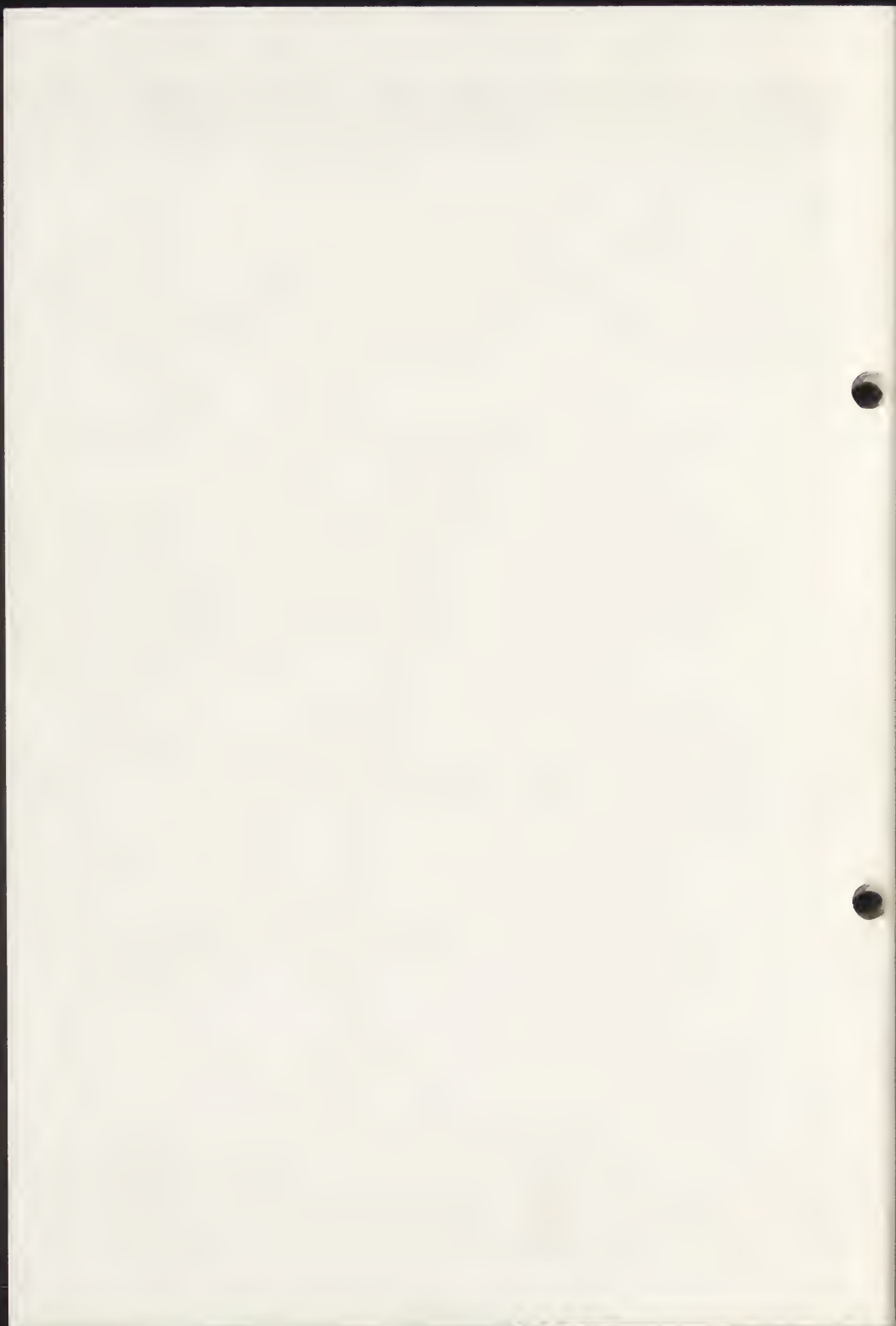
L'introduction dans la méthodologie du traitement de peintures au plâtre de loess en utilisant PBMA-BV en qualité de fixateur essentiel, la fixation préalable de la couche picturale avec le polymère "C-8" n'empêche pas la poursuite du travail, ne complique pas les opérations, mais par contre contribue à la sécurité du procédé principal - de la consolidation.

Les conclusions faites au sujet de la couleur des peintures à condition de l'utilisation du fixatif

essentiel proposé sont confirmées par un examen colorimétrique à l'aide d'un colorimètre photo-électrique à distance élaboré à l'Institut d'Optique Vavilov S.I.

Depuis l'année 1978 la pratique de fixation de la couche picturale sur le plâtre de loess est introduite dans les travaux in situ du Laboratoire de Restauration des peintures murales de l'Ermitage d'Etat.

Les auteurs remercient le collaborateur scientifique en chef de l'Institut d'Optique Vavilov Grouzdeva N.I. et le chef du Laboratoire de chimie de l'Ermitage Guerasimova N.G. qui ont faits les épreuves colorimétriques.



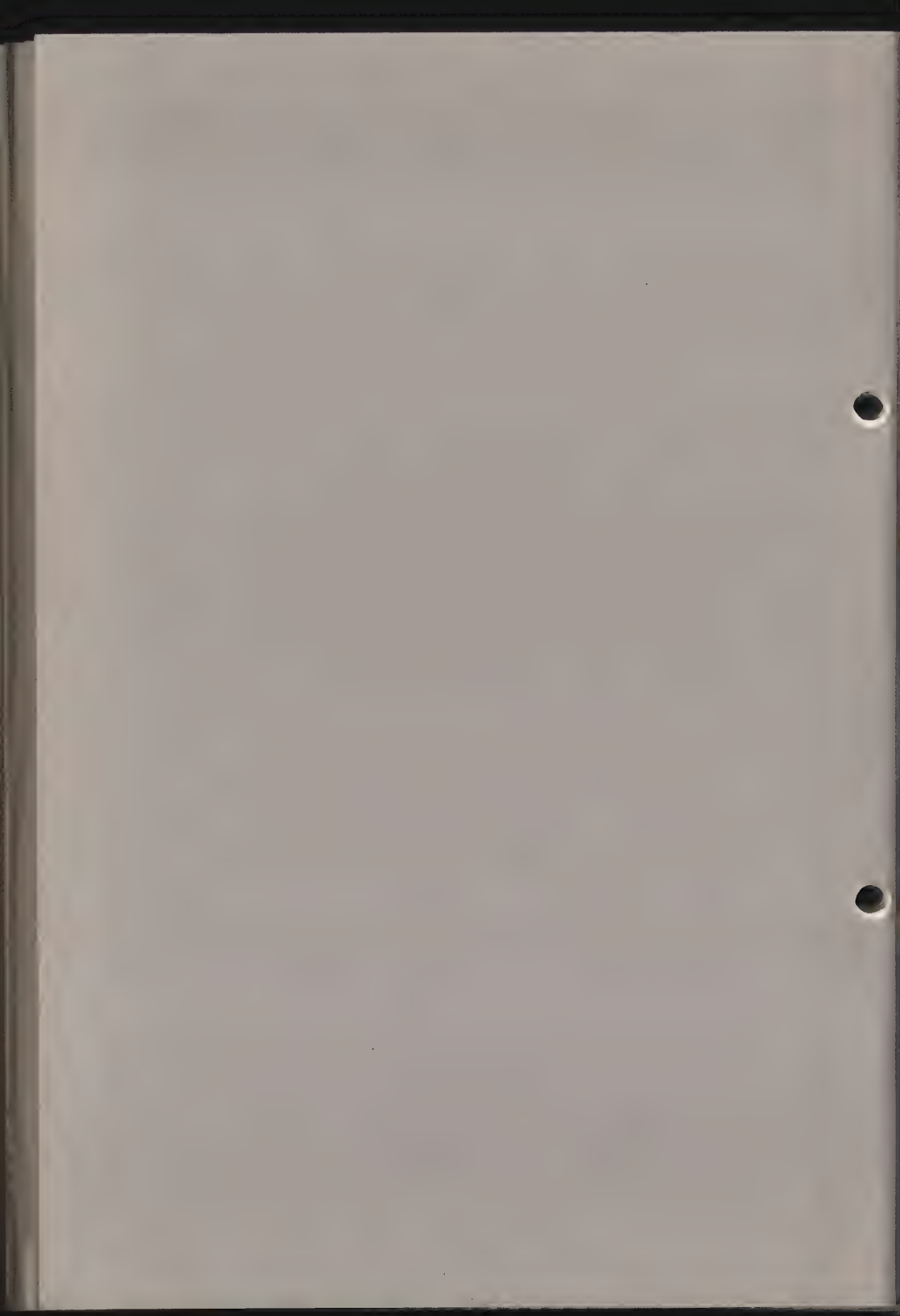
81/15/9

ON THE DETERIORATION OF THE 11TH AND 12TH
CENTURY MOSAICS OF THE BASILICA OF TORCELLO:
PROPOSAL OF A NON DESTRUCTIVE TEST TO
EVALUATE THE MOISTURE OF A WALL

Giorgio Accardo and Vasco Fassina

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Mural Paintings and
Mosaics



ON THE DETERIORATION OF THE 11TH AND 12TH CENTURY MOSAICS
OF THE BASILICA OF TORCELLO: PROPOSAL OF A NON DESTRUCTIVE
TEST TO EVALUATE THE MOISTURE OF A WALL

Giorgio Accardo and Vasco Fassina

Giorgio Accardo
Istituto Centrale del Restauro
Laboratorio di Fisica
Piazza S. Francesco di Paola 9
Roma
Italy

Vasco Fassina
Soprintendenza ai Beni Artistici e Storici di Venezia
Laboratorio Scientifico
Dorsoduro 170
Venice
Italy

ABSTRACT

The moisture content of brick walls is investigated to establish the causes in the deterioration of mosaics in the Basilica of Santa Maria Assunta in Torcello, Venice.

Discontinuities in the mosaic due to restoration made in different centuries, the presence of detached zones of the mosaic from its base, and the height reached by the capillary rising damp on the wall of the "Last Judgement", are studied using thermovision. Humidity due to capillary rise is also identified by weighted measures from cored samples taken from masonry.

On the west wall, quite high values of humidity were found at a 10-12 m height due to water infiltration coming from the rotted roof and gutters.

Cored samples taken from the east wall of the central apse show the capillary rise to be more pronounced with respect to the other walls. This is probably due to the presence of stagnant water in the crypt lying immediately beneath the mosaics of the central apse.

Introduction

During the last decades the rich artistic and monumental patrimony of Venice has undergone a rapid process of deterioration.

According to the traditional environment, the water of the lagoon is in direct contact with the buildings of the town and through capillary action it rises along the walls. Sea water rising into the pores of the materials contains soluble salts which efflorescence on or below the surface of these materials. When the phenomenon of efflorescence takes place on the surface of the building, the salts can be removed by rainwater. The crystallization of soluble salts below the surface is more serious because the internal tensile stresses (blistering) can cause the breakage of the material (1).

Besides capillary rise, some limited condensation of water vapour

can frequently take place in the interior of buildings more so than on the exterior parts.

Surface condensation takes place in the presence of two concurrent conditions: low surface temperatures and high relative humidities of the surrounding air. The first condition is caused by insufficient thermal insulation of walls and roofs and low temperatures of the air, or by excessive external ventilation. The latter condition results from the introduction or production of moisture or insufficient ventilation inside the buildings.

Visitors may increase the relative humidity in a building considerably, because a human produces between 50 and 100 litres of water-vapour per hour.

Marine aerosols, coming from the air-sea interface ejecting sea-salt particles into the air, are transported by the wind and may condense on the cold walls. Gas and particulate pollutants may be removed from the atmosphere and fixed on the surfaces of the walls during the condensation phase.

Since the life of aerosols increases with decreases in temperature, the deterioration of materials may increase in winter (2).

In the present Venetian environment, a marked increase of industrialization and urbanization, taking place in Porto Marghera and Mestre respectively, has upset the precarious traditional environmental equilibrium of the town.

The mosaics of the Basilica of S. Maria Assunta of Torcello present a widespread detachment from the supporting wall (3)

The mosaic representing the "Last Judgement" is divided into six bands and it occupies the whole facade. It was redone twice on different occasions between 12th and 13th century and it represents one of the most important examples of Venetian-Byzantine School.

The state of conservation is not very good, especially in the lower parts, where a widespread detachment from the supporting wall was detected by means of a stethoscopic survey.

The aim of the present study is to individuate the main deterioration processes and the possible heterogeneity present in the masonry and mosaics. In fact, it has been noted that in most of the cases the more serious damages occur in discontinuity points and heterogeneous zones.

For our purpose measurements, based on cored samples from masonry and on the analysis and interpretation of the distribution of surface temperature, were used. In fact, temperature can be detected measuring the radiant temperature by means of the thermovision which is sensitive to infrared radiation (I.R.) (4,5).

Sampling methods and analysis

The core was taken with a low speed drill to reduce water evaporation during the sampling. To minimize the heat produced from friction during the drilling, 2cm cores were removed. In this way evaporation affects only the outside of the sample, since the size of the sample is large enough.

In the majority of cases, the intonaco and the first 10 cm are eli-

minated, while the test samples are between 10-20 cm and between 20-30 cm. The samples therefore show the intrinsic conditions of the wall without traces of the external surface evaporation. Samples, placed in sealed containers, were taken to the laboratory to be weighed (wet weight). They were then placed in an oven at 105 °C for 24 hours to be dried out and then weighed to get the dry weight. They were again placed in the oven and then reweighed until obtaining a constant weight.

Images of radiant temperature were measured with the AGA Thermovision (IR range : 2 to 5.6 μ ; resolution 0.2 °C). The Thermovision is an imaging instrument able to furnish a black and white picture of the object under consideration. Thermal distribution is obtained by means of a scale of grey tones: the black one represents the cold zones, the white one represents the warm zones. The tone corresponds to different isothermal levels. Isothermic levels are individuated with an instrumental skill. At the left of the screen the thermal level is read in conventional units (i.u.) (6).

Preliminary measurements

The use of thermovision for the control of water content in the masonry and of the heterogeneity between mural support and mosaic has been suggested by preliminary tests carried out in the laboratory. On brick samples covered by the traditional layer of intonaco (lime + sand mortar) some tests were carried out simulating both the capillary rise and the detachment between the intonaco layer and the support.

The thermal behaviour of the two cases considered has been viewed from a qualitative standpoint for two reasons: i) the measurement method used allows to examine the difference of temperatures rather than the absolute temperature of single areas, ii) the boundary conditions really representative of the physical state of masonry are not likely to be reproducible in satisfactory manner with laboratory samples.

Therefore, in order to make comparisons, only the results obtained in the case of capillary rising damp (fig.1a) and in the one of detachment between support and intonaco (fig.2a) are reported. In figs.1c and 2b,c thermal profiles related to the vertical crossing the median axis of each sample are represented. Thermal distribution of fig. 1b has been obtained by means of a graphic reduction of single thermograms on which the correspondent isotherms were recorded. Thermal distribution of fig.2a has been obtained after a brick was heated by a constant thermal flux.

Results and discussion

Thermovision measurements are made on the following:

- "Last Judgement" mosaic: internal to facade
- internal part of facade corresponding to the right nave

The exact points, where measurements were carried out, are shown in the floor plan of the Basilica (fig.3).

Fig.4 is photograph of the mosaic of the internal side of facade, and fig.5b gives the corresponding thermovision.

Thermic distribution shows (7):

- i) a triangle-like dark spot with its base at the door and the vertex above the e band
- ii) two circular light spots and two rectangles lower down, which correspond to the four sealed off windows visible from the outside (fig.5c)
- iii) a rectangular spot, intermedium tone, bordering the roof on one side and the triangle on the other.

Excluding the zones around the sealed off windows the distribution curve coincides, within the limit of error, with mosaic works in the different centuries from the 11th century to the more recent restorations (8) (fig. 5a).

To evaluate temperature differences and to determine isothermic surfaces, measurements are made in the horizontal bands (a,b,c,d,e,f) at different height (fig.4).

Thermogram examinations relative to the a,b,c,d bands evidence:

- i) a maximum variation corresponding to 2°C difference in temperature, recorded between the door and the part of the mosaic from the 11th century
- ii) a minimum variation corresponding to a 0.4°C temperature difference between the 11th century mosaics and those from 12 th century.

In the b,c,d,e bands the variations between the two isothermic zones correspond to about a 0.4°C temperature difference.

In the e,f bands, three isothermic levels, which correspond to other zones (8) are identified:

- i) part of the 11th century mosaic
- ii) part of the mosaic done by Salviati and its boundary
- iii) part of the Moro's mosaic and a portion corresponding to the four sealed off windows

The maximum variation measured corresponds to about a 0.6°C temperature difference, the minimum to about a 0.2°C difference.

The distribution trend is determined in our case, from the materials used in the different mosaic works and from various thermic gradients, existing in relation to the sealed off windows due to the difference in thickness of the wall.

In fig.6b the thermogram of the lower part of the mosaics of the "Las Judgement" is reported (fig.6a).

Thermal distribution of fig. 6c has been obtained with a graphic reduction of single thermograms on which the correspondent isotherms were recorded.

The difference of temperature between the isothermal zones always lies between 0.2°C and 0.4°C .

The distribution of horizontal isothermal fronts and vertical gradient measured can be correlated to the presence of capillary rising damp.

To verify this behaviour a thermographic survey and drilling of masonry on a vertical line was carried out in the right nave.

Thermovision observations show a thermal gradient positive with height till about 8 m, where a isothermal zone with a shape approximately of a right-angled triangle (fig.7c).

The geometry of external structure influences the behaviour of isother-

mal surface; in fact, the marked point of discontinuity is coincident with the junction of the roof of the portico, while the thermal gradient of the lower part is dependent on the capillary rising damp in masonry (horizontal isothermal fronts).

The behaviour of this distribution can be directly compared with those reported in figs. 6b,c which is related to the facade of the central nave, and it is located on the continuation of the same masonry. The difference of temperatures were 0.4 and 0.2°C for the lower and upper part respectively. These are in good agreement with measurements obtained, with a thermoresistance, at a depth of 25 cm inside the masonry (table1):

Table 1	
height (m)	temperature (°C)
2	24.8
4	25.0
5	25.2

Drilled samples exhibited a high water content till 3 m (with a peak of 10% at 2 m) which decreases at 4% at 4 and 5 m. The same behaviour is confirmed by surface measurements carried out with an electrical conductivity instrument that till 4 m gave values between 85 and 95, which correspond to wet masonry conditions. These values decrease to 60-70 between 4-5 m showing a transition zone which corresponds to safe limits of moisture. Over the 5 m limit, the wall was dry (9).

The capillary humidity front at this height was also surveyed with thermovision. This front affects the lower part of both the b and c bands of the mosaic. The marble slab under the mosaics (band a of fig.4) prevents evaporation of capillary moisture thus forcing the water to rise inside the wall and to come out higher up in the first two bands of mosaics (10).

A survey in this area, on the adhesion of the mosaic to its base (the support wall), shows widely spread detached areas (fig.8a). An external survey taken between 10-12 meters associated with the corner north-west (fig.5c) gave the following water contents: 2.8%, 3.9%, 4.8% and 7.3%. Also on the north wall, immediately adjacent to the zone, a high water content was found, which was not explainable on the basis of the phenomenon of capillary rise. It is therefore probable that water seeped in from the roof, gutters or some cracks of the wall (11). This was confirmed by a relatively recent leak which caused a rather large vertical crack on the internal side of the mosaic. The highest values, 7.2% and 7.3%, being found at a 20-30 cm depth indicates that wall is quite permanently damp.

Lastly, the thermograms obtained with a 7° telephoto lens are reported in fig.8b,c. The distribution trend can be correlated: i) with the various restorations characterized by the use of heterogeneous materials (compare the geometry of mosaic works attributed to Salvati (fig.5a) and ii) with a stethoscopic survey on the state of conservation made by A. Cassatella.

Besides the internal part of facade was also examined the central apse, where mosaics from the 12th and 13th century representing "The Virgin with Benedicting Child" are found.

The crypt underneath the apse is constantly filled with water. The water level strictly depends on the tide condition of the lagoon. To better understand the possible effect of the stagnant water on the conservation state of the mosaics, bored samples were made at various heights and at a 20-30 cm depth. Results are reported in table 2

Table 2

height (m)	water content (%)
1.5	16.6
2.5	9.7
3.5	3.8
4.5	12.5
5.5	10.4

The depth at which the samples were taken is less likely to be influenced by external conditions such as rain, relative humidity, air, etc. The samples therefore constitute a valid indication of vertical water movements inside the wall and in undisturbed conditions (12). Besides the anomaly at 3.5 m of 3.8% water content, all the others have values quite elevated.

It is clear from the results that capillary rise is of a large magnitude, both for the height reached, and the high water content found at 5.5 m.

Lastly the quantity of water varies between the surface and internal layer, because of the effects of the surrounding ventilation on surfaces which are subjected to evaporation; therefore the higher the rate of evaporation, the lower the content of water.

The vertical trend just observed indicates that the water in the crypt acts as a fundamental and continuous factor in capillary rise movements inside the wall.

Conclusions

Thermic surface distribution were recorded under the different thermodynamic conditions and the differences of temperature among the more significant isothermic zones were measured.

By thermovision it was possible to compare the thermic behaviour of more than one part of the same structure and to evidence existing heterogeneity. It was possible to individuate:

- i) discontinuity in the application of the mosaic which by other means were identified as restorations and additions to the original made in different periods
- ii) heterogeneity due to difference in the thickness of the wall in relation to the sealed off windows and to raised or detached areas between the mosaic and the base (its foundation)
- iii) presence of humidity in the wall caused by capillary rise even if no quantitative indication was given regarding the percentage of water present.

A quantitative examination for water content in the walls was carried out by gravimetric methods on bored samples. Results obtained confirm the presence of the phenomenon of capillary rise in the west wall of

the "Last Judgement" and, within the limits of instrumental errors, data obtained with thermovision.

The height of the capillary rise is determined not only by the following factors: the size of the brick pores, the level of water-bearing stratum, the quantity and nature of soluble salts present in the water and the wall; but also by surface evaporation rate of water which in this case is limited by the presehce of marble slabs located under the mosaics.

Still on the west wall, high values of humidity were found at a 10-12 m height which are not explained by capillary rise, but which are due to water seepage, in correspondence to masonry cracks, during rains.

Lastly the bored-sample from the east wall of the central apse shows that humidity was caused by capillary rise of the stagnant water in the crypt lying under the apse.

The harmful effect of the crypt is especially revealed in the course of microclimatological tests made inside the Basilica. In fact, the crypt constitutes a large evaporation source which influences the atmosphere inside the Basilica, particularly, in the left nave (13). Permanent removal of the water in the crypt would eliminate the microclimatological changes inside the Basilica which are especially large during summertime. Moreover it would minimize capillary rise decreasing the height reached to a level below that of the mosaics.

Acknowledgements

For the precious contribution to the study authors wish to thank:

- dr. A. Bonarrigo (Soprintendenza ai Beni Artistici e Storici di Venezia) for the gravimetric measurements
- Mr. A. Ongaro for the microclimatological measurements
- Mr. F. Orfanò for the photographic part (I.C.R. Roma)
- Mrs. A. Gorini and B. Pompili (Istituto Centrale del Restauro di Roma) for the graphic part

A particular thanks to the International Torcello Committee and to the President Sir Ashley Clarke who made the financial support for the realization of the study.

References

- 1) V. Fassina, A survey on air pollution and deterioration of stone-work in Venice, *Atmos. Environ.* 12 (1978) 2205-2211.
- 2) G. Torracca, Controllo del microclima negli edifici monumentali di Venezia per la conservazione delle opere d'arte, II Convegno Internazionale "Il problema di Venezia", Divisione Urbanistica del Comune di Venezia.
- 3) V. Fassina, Preliminary results of the air pollution survey inside the Basilica of S. Maria Assunta of Torcello in Venice, European Conference on Environmental Pollution, 18-19 December 1980, Frankfurt, West Germany.
- 4) G. Urbani, Applicazione della termovisione nel campo della conservazione delle opere d'arte, in G. Urbani (ed.) "Problemi di Conservazione" 317-327, Ed. Compositori, Bologna, 1973.
- 5) G. Cesini, F. Gori, G. Guattari and G. Lucarini, Thermal methods for painting diagnostics, 7th I.I.C. Congress, Oxford, Sep. 1978.
- 6) G. Accardo, D. Camuffo and G. Ferrari, Indagini micrometeorologiche all'interno della Cappella degli Scrovegni, Atti del Seminario "Apporto della meteorologia nel controllo e nell'abbattimento dell'inquinamento atmosferico, Roma 8-10 Nov. 1978, C.N.R. pubblicazioni, Roma, 1978.
- 7) G. Accardo, D. Artioli, Rilevamento termografico all'interno della Basilica di Torcello, progress report, Istituto Centrale del Restauro, Roma 1978.
- 8) I. Andreescu, Torcello - III la chronologie relative des mosaïques parietales, *Dumbarton Oak Papers*, XXX (1976), New York.
- 9) V. Fassina, Misure di umidità e di sali solubili nelle murature di chiese ed edifici: 3 casi, Incontri sulle tecniche del restauro "Risanamento degli edifici del centro storico di Venezia dai danni dell'umidità" 5 nov. 1979, Venezia.
- 10) V. Fassina, Indagine micrometeorologica all'interno della Basilica di S. Maria Assunta di Torcello, Progress report n.3 16/1/80, Soprintendenza ai Beni Artistici e Storici di Venezia, 1980.
- 11) V. Fassina, Controllo del microclima e rilevazione igrometrica della muratura della Basilica di S. Maria Assunta di Torcello, Progress report n.2 28/9/79, Soprintendenza ai Beni Artistici e Storici di Venezia, 1979.
- 12) V. Fassina, Rilevazione igrometrica della parete est della Basilica di S. Maria Assunta di Torcello, Progress report n.5 26/9/80, Soprintendenza ai Beni Artistici e Storici di Venezia, 1980.
- 13) V. Fassina, Indagine micrometeorologica all'interno della Basilica di S. Maria Assunta di Torcello: Risultati della 4a campagna, Progress report n.4 26/5/80, Soprintendenza ai Beni Artistici e Storici di Venezia, 1980.

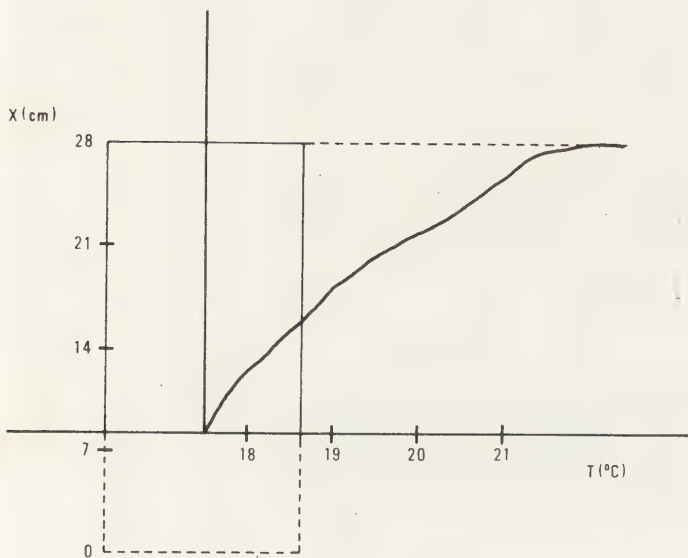
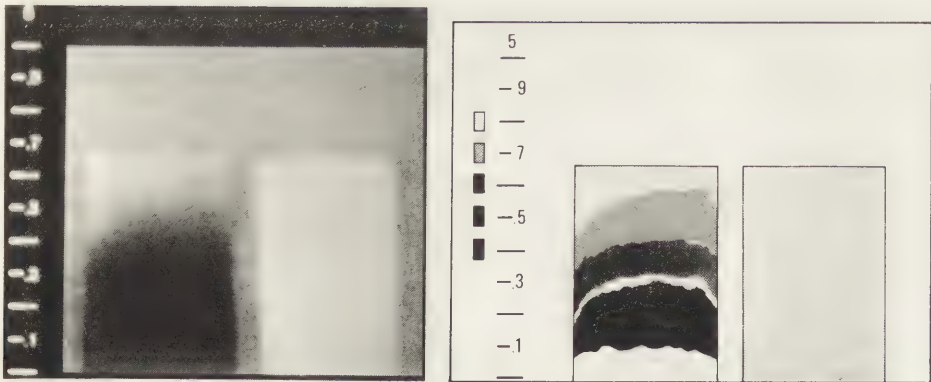


Fig.1 a) Comparison between the thermovision of a brick drenched with water by means of capillarity (on the left) with the one not drenched (on the right)
 b) Isothermal behaviour of the same brick samples
 c) Vertical thermal profile crossing the median axis of the brick drenched with water

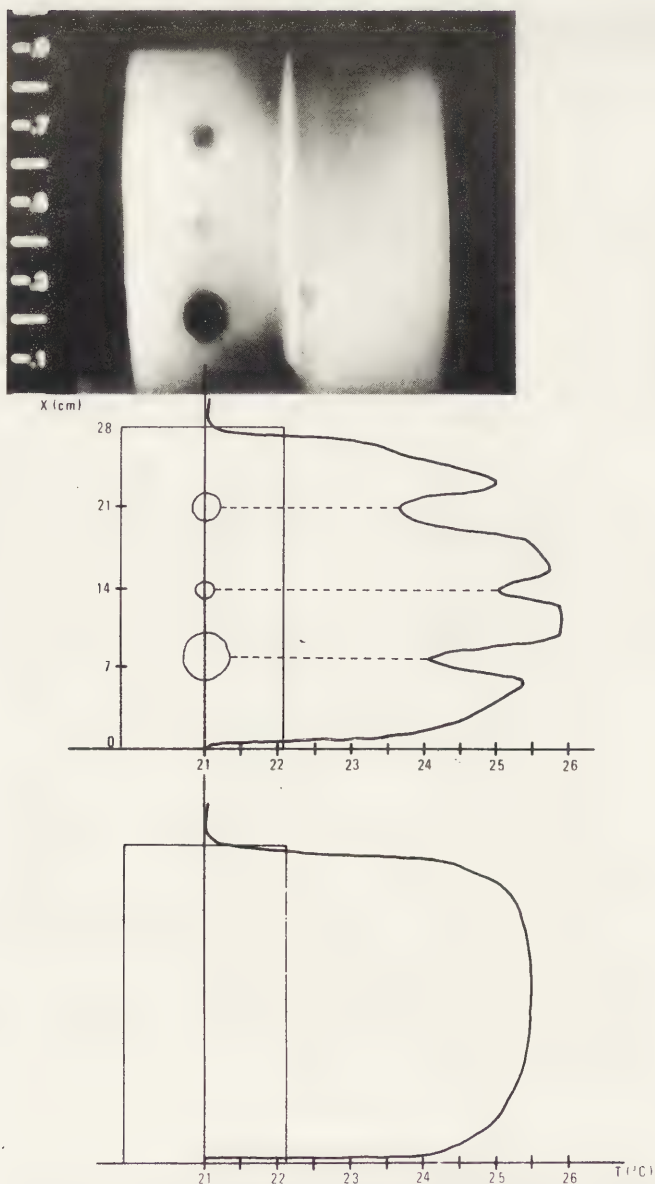


Fig.2 a) Surface temperature distribution for a sample prepared with some detachments between the support and intonaco and for another one with adherent and homogeneous intonaco in phase of cooling
 b) Vertical thermal profile crossing the median axis of a sample prepared with detachment zones during the cooling phase
 c) Vertical thermal profile crossing the median axis of a sample prepared with a homogeneous intonaco during cooling phase

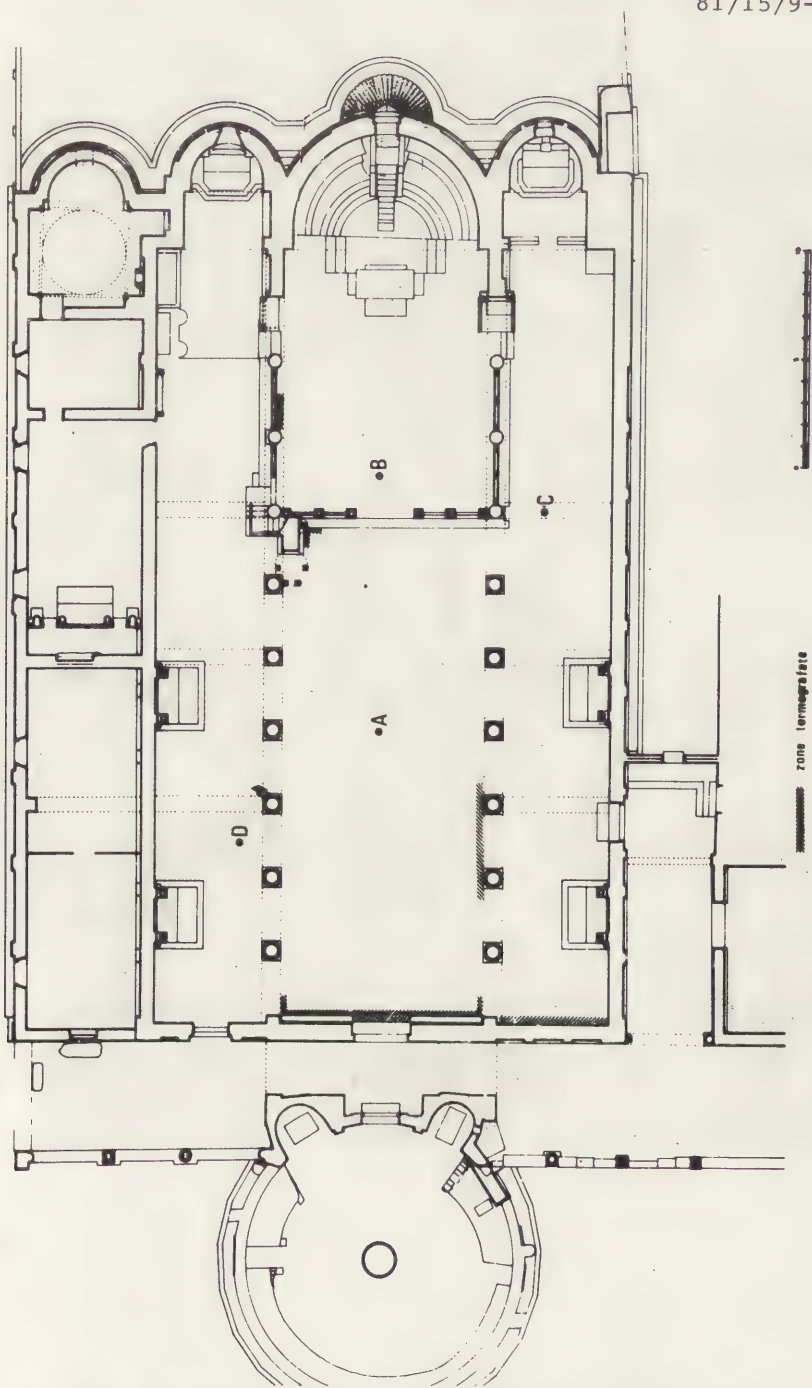


Fig.3 Plan of the Basilica with the thermographic zone and points of observation

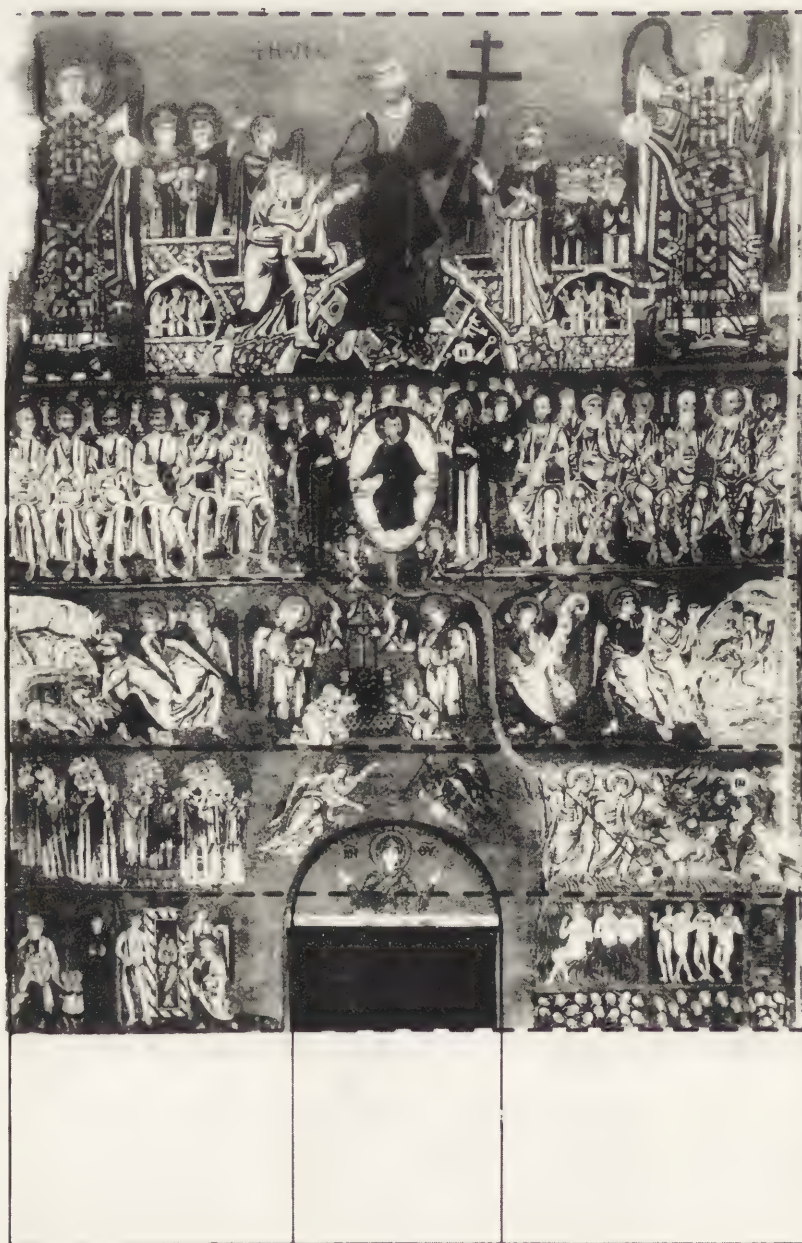


Fig. 4 The mosaic of the "Last Judgement" divided into six bands

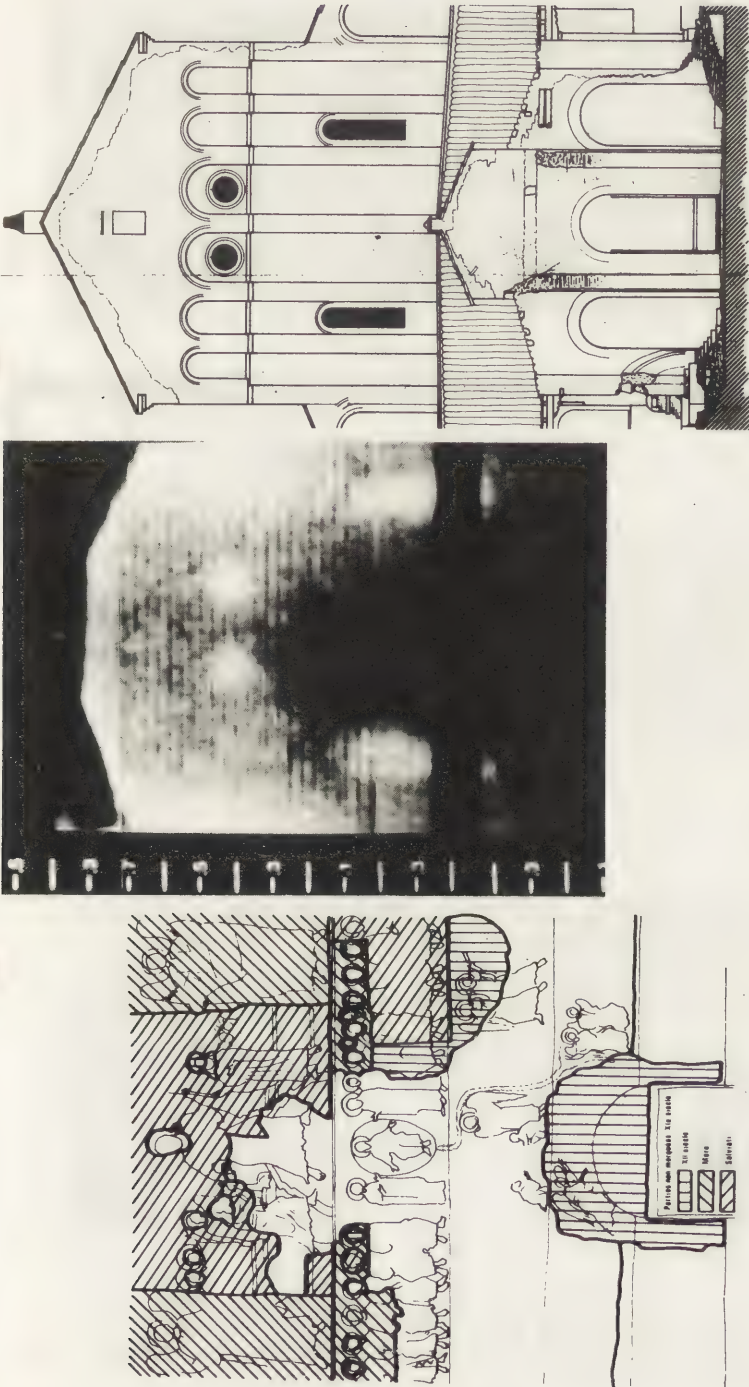


Fig. 5 a) Zonal mapping of restorations in the different periods

b) Thermovision of the mosaic of the "Last Judgement"

c) The four sealed off windows located on the facade of the Basilica and individuated by thermo vision of fig. 5b

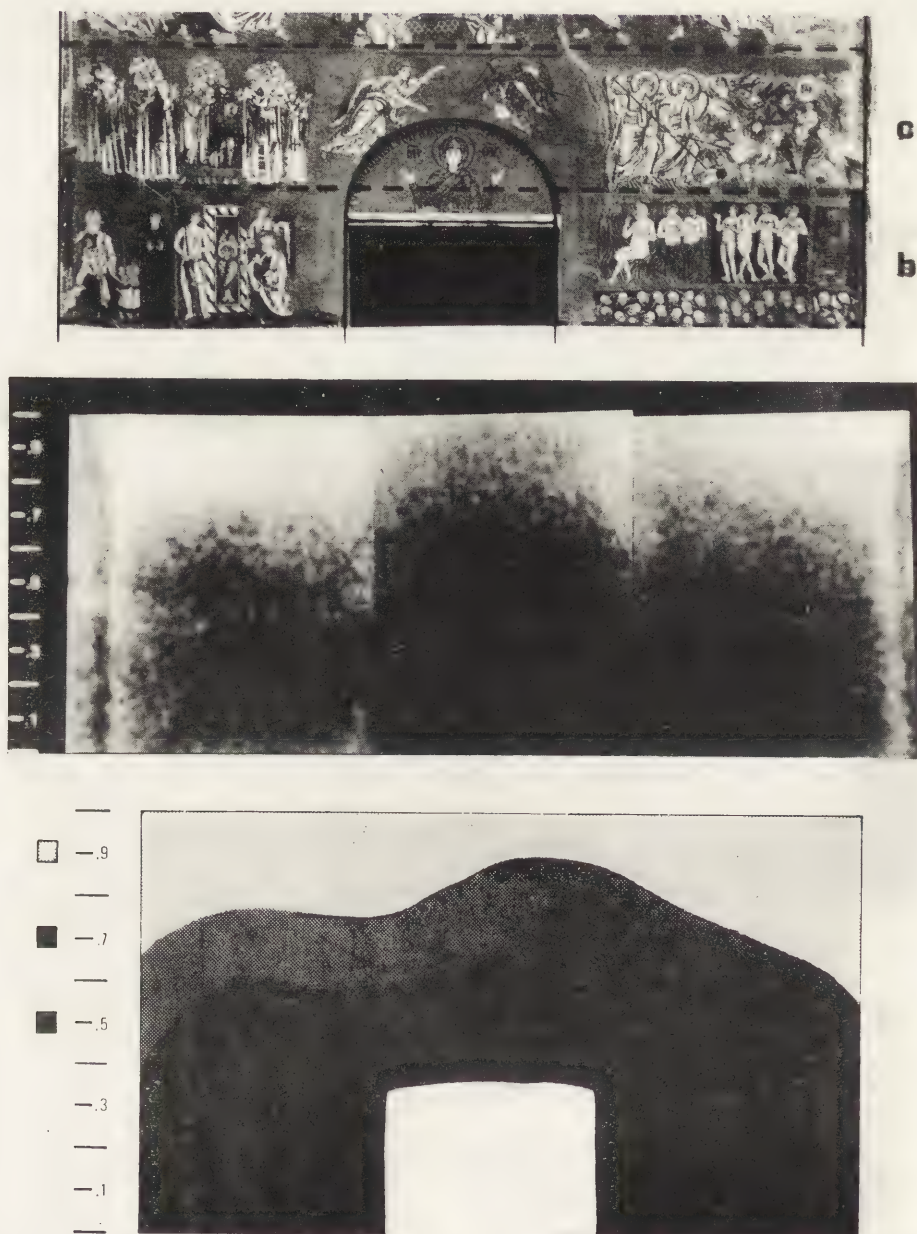


Fig. 6 a) The lower bands of mosaic
 b) Thermovision of the b and c bands of the mosaic
 c) Horizontal isotherms individuating the capillary rising damp behaviour

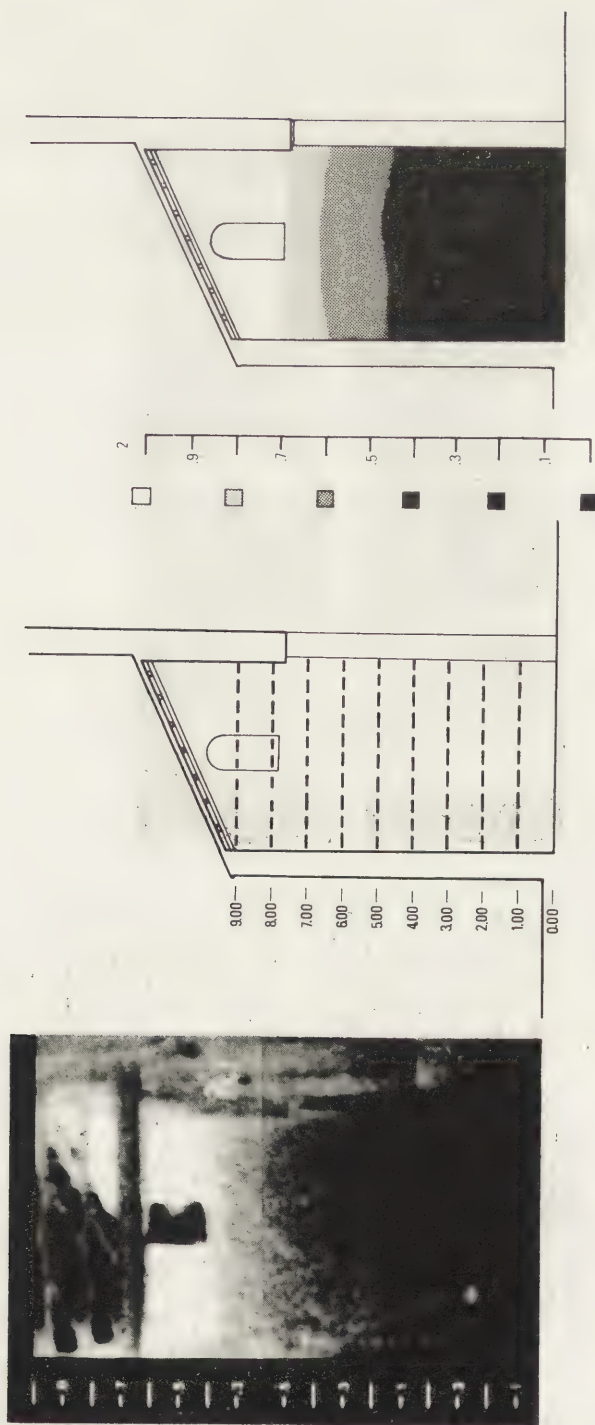


Fig. 7 a) Thermovision of the lower part of the right nave
 b) The right nave with relative heights
 c) Horizontal isotherms individuating the capillary rising damp (compare with fig. 6c and percentages obtained from drilled samples)

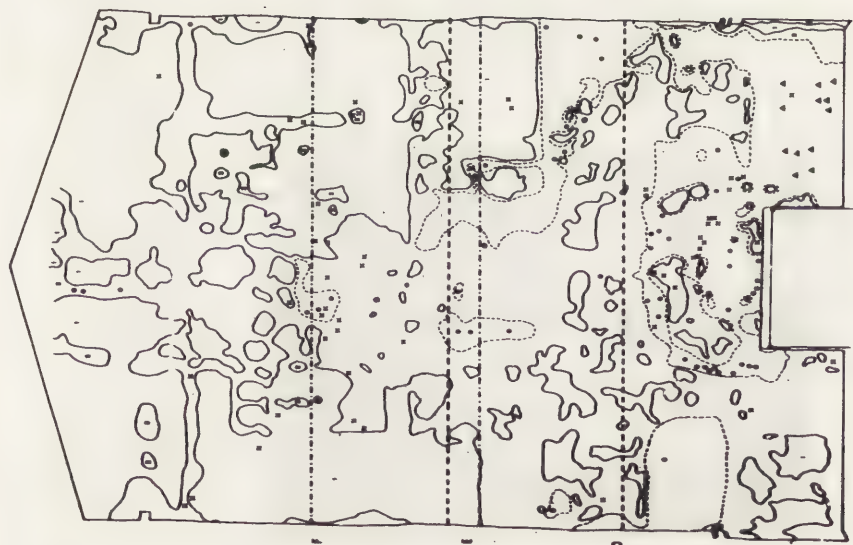


Fig. 8 a) Maps showing: 1 unaffected areas, 2 intermedium detached zones, \square greatly detached zones, Δ visible clamps, x clamps detected magnetically, \bullet flexible points
b) Thermal fields identifying detachment zones

PROTECTIVE COATINGS, TRADITIONAL AND MODERN

Coordinator : R. Feller (USA)

Assistant coordinator: E. de Witte (Belgium)

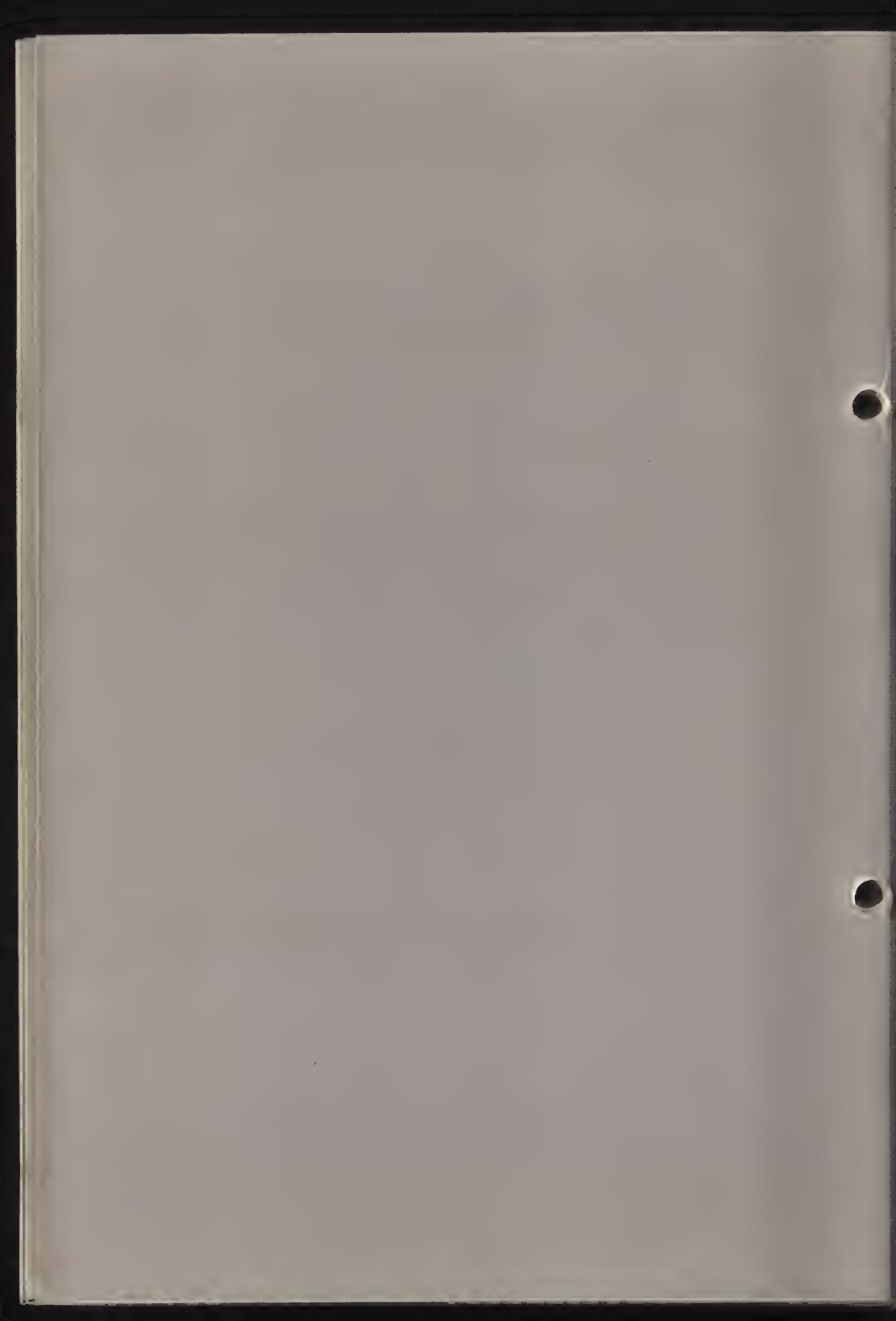
Members : N. Baer (USA)
R. Lafontaine (Canada)
L. Masschelein-Kleiner (Belgium)
I.V.Nazarova (USSR)
N.H.Tennent (UK)
L. Van Zelst (USA)

Programme 1978-1981

The principal effort of the working party (working group) for 1978-1981 will be to exchange views in an effort to agree upon acceptable standards, 1. for "strength" of solvent needed to dissolve thermoplastic resins, 2. for intrinsic viscosity or "Viscosity grade" of resins, 3. for lightfastness (ISO R105 bluewool fading standards), 4. for standard resins (butyl methacrylate, or methylacrylate-ethyl methacrylate copolymer or vinyl acetate), 5. Oddy test for corrosive vapors.

A circular letter will be sent to various laboratories to learn of tests that may have acceptance and utility in other countries. It would be expected that colleagues from other countries would join the working group if they respond favorably to the letter.

1. Testing of emulsion adhesives (Baer).
2. Use of inhibitors in varnishes (Lafontaine).
3. Testing of water-soluble resins (Van Zelst, Feller).
4. Testing of epoxy resins (Tennent).



81/16/1

DEVELOPMENTS IN THE TESTING AND APPLICATION
OF PROTECTIVE COATINGS

Robert L. Feller

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Protective Coatings,
Traditional and Modern

DEVELOPMENTS IN THE TESTING AND APPLICATION OF PROTECTIVE COATINGS

Robert L. Feller

Center on the Materials of the Artist and Conservator
Mellon Institute
Pittsburgh, Pa. 15213
USA

Summary

An overview of progress in the past several years indicates that outstanding advances have been made in the conservator's knowledge of solvent power owing to an increased appreciation and understanding of the concept of solubility parameters. Objective investigations are increasingly being conducted on the ease of removal of aged coatings. A so-called "hard-edge" phenomenon frequently observed in these studies, is noted in which the coating dissolves primarily by gradual dissolution of the surface of the resin. An extensive 1981 review of the photochemical reactions of methacrylate polymers under visible and near-ultraviolet radiation is cited. As to the immediate future, it is suggested that the field will be devoting more attention to testing of thermosetting resins and of additives such as antioxidants and ultraviolet absorbers. Standard coatings that possess both excellent and intermediate properties will be needed.

Introduction

The ICOM Committee for Conservation and its predecessor, the Committee on Laboratories, has long served a valued role in international conservation efforts by providing a forum where particular needs of research, review, and evaluation-of-status could be expressed and more precisely defined, and where triennial reviews of the status-of-progress could be presented regarding more than twenty-five special areas of interest. As Coordinator of the Working Group on Protective Coatings - Ancient and Modern, I shall attempt to point out a number of significant developments regarding this subject and to draw attention to some of the still-unresolved problems.

Solvents and Solvency No Longer a Problem

Much of the attention of this working group in the past has been devoted to questions regarding solvent-type varnishes prepared with natural or synthetic thermoplastic resins, particularly those applied as

picture varnishes. Perhaps one reason why so much attention was given to this subject in the past is that picture varnishes posed serious problems to the conservator of paintings owing to their marked tendency to discolor and to become difficult to remove with reasonable safety. With the advent of the principles of solubility parameter, the conservator has gradually come to understand and to master the more or less subjective concepts of "strong" and "mild" or "weak" solvents.^(1,2,3) Of particular importance was a clear demonstration of the fact that the maximum solvent action occurs when the solubility parameter of solvent and resin are the same. Thus, solvents will have little action at all if their solubility parameters are very much above or very much below the solubility parameter of the resin or dried-oil film that the conservator is attempting to dissolve or swell. The understanding of this behavior was immediately applied to advantage by the conservator of paintings. For example, during the treatment of a paint structure varnish that was found to be soluble in solvents traditionally considered to be "mild" (such as petroleum solvents), it was shown that such paintings could often be effectively coated over - perhaps in a "facing" procedure prior to lining or transfer - using adhesive materials that were soluble in highly polar solvents such as alcohol. Following treatment of the painting, such temporarily employed stratagems could again be reversed or "undone" with highly polar solvents that had little tendency to dissolve the non-polar-solvent-sensitive coating below.

Ease of Removal of Photochemically Aged Resins

Although three parameters are currently considered necessary to define the solubility characteristics of solvents and resins fully, the author has proposed a series of mixtures of cyclohexane, toluene, and acetone that provides a convenient one-dimensional scale of solvent power.^(4,5) This series of solvents was used by the Center in 1975 to measure the increased difficulty of removal of various types of varnishes following exposure to "daylight" fluorescent lamps.⁽⁶⁾ Among the interesting results of this investigation was the finding that dammar and mastic varnishes reach a limit in the polarity or "strength" of solvent needed to remove them; thus, if an old varnish cannot be removed with a "test-mixture" of 50/50 toluene/acetone by volume, we can be reasonably sure that it cannot have been based on simple dammar or mastic resin. A second result of this investigation indicated that the solubility characteristics of polyvinylacetate homopolymers and Acrylo-B-72 (a copolymer of methacrylate and ethyl methacrylate)⁽⁷⁾ would remain practically unchanged for more than 20,000,000 footcandle hours of illumination by "daylight" fluorescent lamps. At the end of such an exposure, they could still be removed in a solvent mixture of slightly lower polarity than toluene (80/20 toluene/cyclohexane by volume). It can be estimated that this is on the order of the total amount of exposure that can be encountered on the wall of a skylight-illuminated gallery in about 200 years.

We are pleased to report that this solvent series - intended primarily as a standard of reference during solvency testing and not to be

used for the lengthy procedure of stripping of varnish from paintings - has been used in research investigations reported by several colleagues in the past three years.(8,9,10)

The Hard-Edge Phenomenon in Removal of Aged Coatings

There is an aspect of varnish removal that has received little attention yet which is of practical interest. In our laboratory, we call it the "hard-edge" phenomenon and have observed it particularly in the attempt to dissolve certain resins following accelerated-aging tests, especially the hard and brittle types. When the resin has been coated on a sheet of metal or glass for laboratory tests, we have frequently found, when attempting to remove the thoroughly dry or aged film with cotton swabs dipped in solvent, that the resin develops cracks much like mud-dried cakes and, as dissolution progresses, the cracks widen; the areas of resin - like so many cakes of ice - persist, with very hard edges which pull against the cotton swabs. The progress of dissolution appears somewhat as shown in Figure 1.

The explanation may be as follows: resins can dissolve in two essentially different modes. Like a cake of ice or a salt crystal dissolves in water, some materials tend to dissolve away by an erosion of the outer surface. This is characteristic of the resins that exhibit the "hard-edge" phenomenon. The result can be a slow process, annoying to a conservator who may be attempting to remove such a coating. On the other hand, many polymeric materials tend to swell throughout their entire volume and then to gradually pass into solution as swelling becomes increasingly advanced. Many polymeric coatings such as polyvinylacetate or Acryloid (Paraloid) B-72 react in this latter fashion.

It is the opinion of the author that the hard-edge phenomenon is most often encountered in natural resins and synthetic polymers that are below their second-order transition temperature during the attempt to dissolve them. The phenomenon occurs in thermoplastics that have a high pencil hardness (which is perhaps to say much the same thing as to state that the second-order-transition temperature is high). It is especially apparent in those resins that develop cracks during the process which later tend to expand and to reveal hard edges as the solvent action gradually erodes the outer surface. The hard-edge phenomenon may or may not prove to be of interest to the conservator, but it is mentioned because it has been particularly noticeable during the accelerated-aging testing of various resins. We believe that our tentative explanation (hard resins that dissolve primarily from the outer surface with practically no swelling) is a reasonable one and have found that raising the temperature of the coatings, often only slightly (intending to bring them above their second-order-transition temperature) often alleviates the problem.

Review of Action of Light on Methacrylate Polymers

A detailed review of the photochemical behavior of methacrylate thermoplastics is scheduled to appear at the time of this writing.(11) This review of the work of the Coordinator and his colleagues that has

been sponsored for more than thirty years at Mellon Institute by the National Gallery of Art and the Andrew W. Mellon Foundation includes hitherto unpublished data and coordinates numerous experimental findings on the effects of wavelength, temperature, and polymer composition that have appeared in a variety of journal publications over the years. Many of the reports of various workers that have appeared in the chemical literature concerning the degradation of methacrylate and acrylate polymers have involved the use of very short wavelengths of ultraviolet radiation (which tend to cause methacrylate polymers to depolymerize and yield a high percentage of monomer) or have involved the use of high vacuum or inert atmospheres, conditions which are of little interest to the conservation scientist. Nonetheless, where reports in the literature do relate to the conservator's interest and concern for the stability of these materials, they have been cited in the review; a total of thirty-one references is given in the bibliography.

An interesting technique for speeding up the destructive effects of peroxide formation and subsequent deterioration in coatings, cited in this review, is the work of Barton, who added known amounts of benzoylperoxide to methacrylate resins in order to speed up their tendency to crosslink.⁽¹²⁾ The intentional addition of peroxide might be used in accelerated-aging tests for those materials that deteriorate through a mechanism involving peroxide intermediates.

Analysis of Traditional Resin-Oil Varnishes

Methods of liquid-vapor chromatography are yielding valuable information on the constitution of traditional coatings based on the thermal processing of resins and oils. Moreover, mass spectrographic methods are being introduced that will allow extremely small samples of an organic coating to be characterized. I have asked other speakers at this meeting, who are directly involved with these important new developments, to speak on the investigations taking place in their laboratories.

Problems to be Examined in the Future

An increasing number of conservation-oriented laboratories are now in a position to investigate the chemical and physical deterioration of protective coatings, as evidenced by the number of articles on the subject published since the Zagreb meeting in 1978.^(8,9,10,13) In such evaluation studies, there is the presumption of standards of reference, whether they are formally established yardsticks for durability and performance, or whether they are assumed or generally accepted criteria. Thus, in the area of thermoplastic resins, the tacitly accepted standard resin for picture varnishes in terms of long-term solubility and lack of yellowing is perhaps Acryloid (Paraloid) B-72, and a standard for desired initial appearance is dammar. A suitable monitor for comparing the rate of crosslinking on exposure to light is either poly(n-butyl methacrylate) or a 50/50 copolymer of n-butyl and isobutyl methacrylate, easily available and of documented tendency to crosslink.⁽⁴⁾ We are now encountering more and more reports on the testing and evaluation of thermosetting resins, both for interior and exterior applications exemplified by the work on epoxy resins by Tenent⁽¹³⁾ and by the

studies being carried out by colleagues at the Canadian Conservation Institute. I also believe that there will be considerable interest in the future in investigating certain silicone-based thermoplastic resins (and possibly air-drying thermosetting types) which were not commercially available only a few years ago.

By what criteria do we judge these new categories of resins? The field needs representative polymers to serve as "controls" and standards of reference for such studies. The establishment of performance standards should be one of the objectives of this working group.

Other polymer or resin characteristics which remain to be investigated include the question of the minimum brittleness (flexibility or elongation at break) desired in a picture varnish. What method of determination and numerical limits should be specified? In addition, there have long been arguments about the appearance of various clear protective coatings, particularly when initially applied as picture varnishes, concerning which the field has practically no objective data. The causes of the surface appearance differences - whether they are attributable to fundamental properties of the polymers or whether they can be, or perhaps have been in some workshops, practically eliminated by changes in formulation or application techniques, remain largely unexplained. It is encouraging to find that a report in this area, by investigators at the Institut royal du Patrimoine artistique in Bruxelles, will be presented here at this meeting.⁽¹⁴⁾

Mr. Raymond Lafontaine will review at this meeting the extensive investigations of antioxidants and ultraviolet absorbers in varnishes that are being conducted at the Canadian Conservation Institute. Undoubtedly such additives will become of increasing interest and utility to the conservator in the coming years.

References

1. Stolow, N., "The Action of Solvents on Drying-Oil Films", J. Oil and Colour Chemists' Assoc., 40 (1957), 337-402; 438-499.
2. Feller, R. L., Stolow, N. and Jones, E. H., On Picture Varnishes and their Solvents, Cleveland, Press of Case-Western Reserve University, Revised edition, 1971.
3. Torracca, G., Solubility and Solvents for Conservation Problems. Rome International Centre for the Study of the Preservation and Restoration of Cultural Property, 1975.
4. Feller, R. L., "Standards in the Evaluation of Thermoplastic Resins", ICOM Committee for Conservation, Zagreb meeting, 1978, paper 78/16/4.
5. Feller, R. L., "The Relative Solvent Power Needed to Remove Various Aged Solvent-Type Coatings", in Conservation and Restoration of Pictorial Art. N. Brommelle and P. Smith, Ed., Butterworths, London (1976), pp. 158-161.
6. Feller, R. L. and Curran, M., "Changes in Solubility and Removability of Varnish Resins with Age", Bulletin American Group-IIC, 15, No. 2 (1975), 17-26.
7. DeWitte, E., Goessens-Landrie, Goethals, E. J. and Simonds, R.,

- "The Structure of 'Old' and 'New' Paraloid B-72", ICOM Committee for Conservation, Zagreb meeting, 1978, paper 78/16/3.
8. Raft, K., "An Examination of the Value of Re-forming Technique in Practice", Studies in Conservation, 25 (1980), 137-140.
 9. DeWitte, E. and Goessens-Landrie, "The Influence of Light on the Appearance and the Stability of Varnishes", Bulletin Institut royal du Patrimoine art., 17 (1978-9), 106-121.
 10. Lafontaine, R. H., "Effect of Irganox 565 on the Removability of Dammar Films", Studies in Conservation, 24 (1979), 179-181.
 11. Feller, R. L., Curran, M. and Bailie, C., "Photochemical Studies of Methacrylate Coatings for the Conservation of Museum Objects", in American Chemical Society Symposium Series No. 151, 1981, in press.
 12. Barton, J., "Peroxide Crosslinking of Poly(n-alkyl Methacrylates)", J. Polymer Sci., A1, 6 (1968), 1315-1323.
 13. Tenent, N. H., "Clear and Pigmented Epoxy Resins for Stained Glass Conservation: Light Aging Studies", Studies in Conservation, 24 (1979), 153-164.
 14. DeWitte, E., Goessens-Landrie, Goethals, E. J., Van Lerberghe, K. and Van Springel, C., "Synthesis of an Acrylic Varnish with High Refractive Index", ICOM Committee for Conservation, Ottawa, 1981.



FIGURE 1

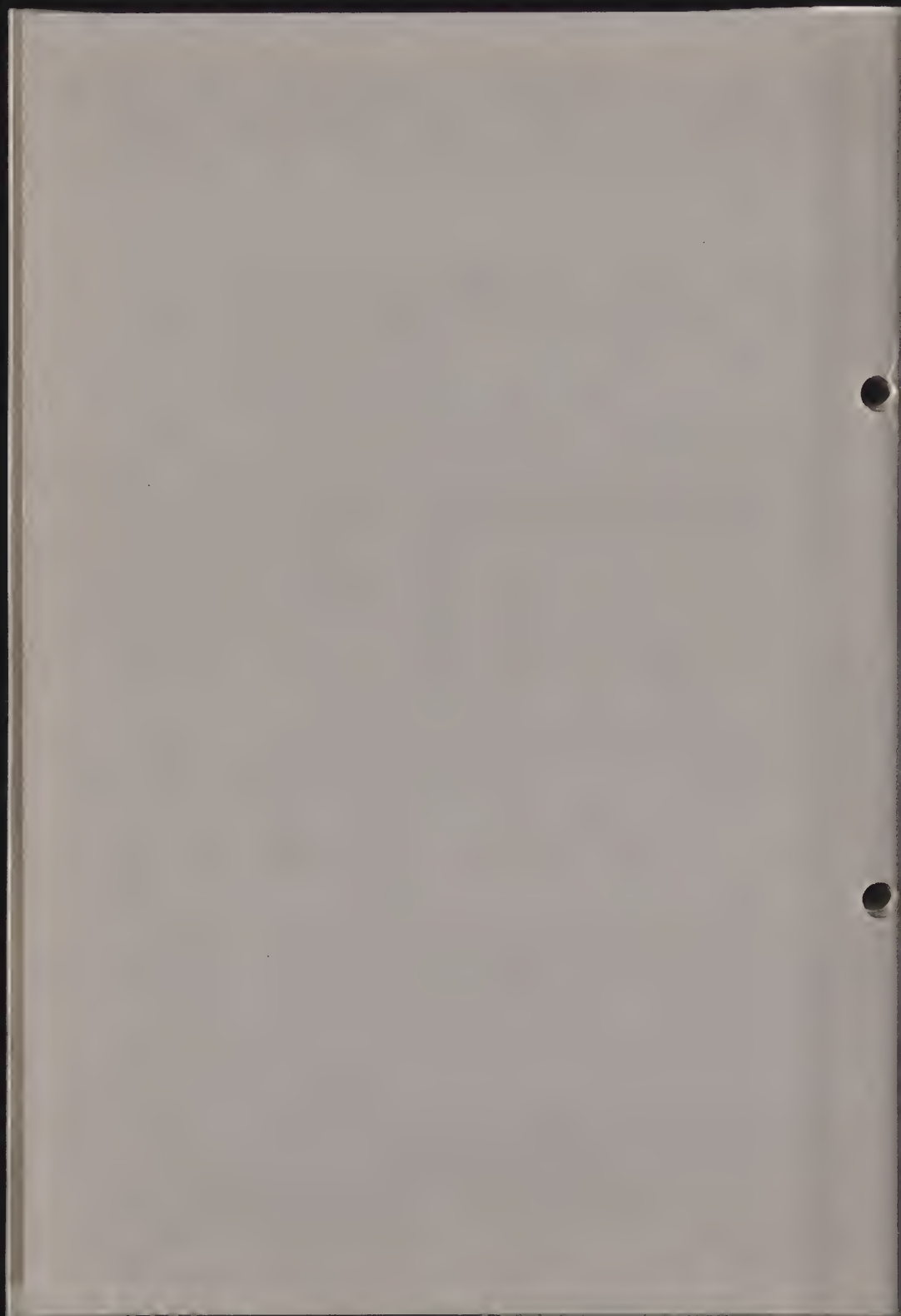
STAGES IN THE DISSOLUTION OF A VARNISH THAT EXHIBITS THE
HARD-EDGE PHENOMENON, DISSOLVING AWAY PRIMARILY FROM
THE OUTER SURFACE

A REVIEW, WITH ILLUSTRATIONS, OF METHODS
APPLICABLE TO THE ANALYSIS OF RESIN/OIL
VARNISH MIXTURES

R. White

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Protective Coatings,
Traditional and Modern



A REVIEW, WITH ILLUSTRATIONS, OF METHODS APPLICABLE TO
THE ANALYSIS OF RESIN/OIL VARNISH MIXTURES

R. White

Scientific Department
National Gallery
Trafalgar Square
London WC2N 5DN
Great Britain

ABSTRACT:

A review of the analytical procedures currently employed in the laboratory of the Scientific Department at The National Gallery for the analysis of resin-oil varnish mixtures is given. In addition, critical comments are offered on techniques which have been examined, but were found to be either partially or totally unsatisfactory.

An outline of the application of such methods is given, a fuller treatment of which, together with specific examples, will be made at the Conference. Emphasis is placed upon gas chromatographic methods and gas chromatography linked with mass spectrometry.

The underlying difficulty that has hampered the organic chemist in his attempts to adequately characterise the composition of varnishes is the inherent complexity of natural products from which they are confected. This coupled with the changes effected by oxidation and radiation damage, particularly marked in the case of varnish surface coatings, together with the limitations on sample size, all serve to take such analyses well beyond the realm of the small museum laboratory. At one time, the thought of simple 'spot tests', to characterise the main component types of these mixtures together with checks on physical properties of the sample, seemed to be within the realms of possibility. However, during the last few decades as we begin to learn a little more about such natural products, this hope has faded into obscurity. Straightforward, one-procedure methods, whether instrumental or otherwise, cannot come to our aid in this matter. Infra-red spectroscopy, conventional or A.T.R., though very convenient and within limits non-destructive, may prove useful when examining relatively uncomplicated varnish mixtures in a fresh state. In particular, this method is ideal for the analysis of modern, synthetic varnish formulated on acrylics, cyclohexanol/one polymers and polyvinyl acetate components. However, when dealing with aged plant material, only rarely does one obtain a spectrum with sufficient detail to allow identification of specific indicator compounds within the

mixture, thereby pointing to a possible source of the ingredients.

In general, as a result of cross-linking and scission such a multiplicity of bond-types result, that the absorption bands merge into a series of broad envelopes, thus precluding the possibility of extracting meaningful data on the absorption maxima.

Careful examination of the soluble portion of a varnish, after swelling and soaking in, say, ether/methanol, will produce a slight improvement in detail of the spectrum as a result of exclusion of higher polymer alone. Yet further improvement may be brought about by methylation of the sample, to esterify any free fatty and resin acids. Even so, it may well be impossible to come to any conclusions as to the components contained therein. Indeed, frequently it is impossible to tell whether the resin present is diterpenoid or triterpenoid!

However, where an inclusion of beeswax has been made (such as in a matt varnish layer), infra-red examination will often permit identification of this material with reasonable facility. (Ref. 1) Indeed, in this laboratory, not only wax in varnish layers, but small amounts of wax surface polish have been determined by this means, though this technique has been backed up by gas chromatography since minor additions of other waxes can quite easily be missed by spectroscopy alone. (Ref. 2)

Faced with a mixture of components, some monomeric, others oligo- or polymeric, it is clear that the chemist must attempt some form of separation into fractions. Once this has been accomplished he can then investigate the fractions in turn, or use methods which are transparent to some of the less useful components. When we speak of separation methods, the most powerful that springs to mind, in this context, is that of chromatography.

Thin-layer chromatography has been applied to the analysis of resin components in this laboratory. It appeals, in that the capital cost of equipment and plates is minimal. With reasonable skill, the chemist can attempt an analysis. It has been the experience of the author that reasonable results can be obtained for individual resins or certain combinations of resins. However, when dealing with aged films or resin/oil mixtures that have been aged, the method frequently leaves a great deal to be desired. Once again, polymeric materials and polar oxidation products conspire to obscure and hinder the detection of useful indicators. In addition, tlc is rarely capable of resolving mixtures into anything other than overall compound classes (e.g. axial and equatorial alcohols, ketones, acids, etc.). Hence, great care must be taken in interpretation of the results. Certainly, it is essential to exclude as much of the polymer and polar components as possible. Failure to do so, will cause a marked smearing of the chromatogram, which will hide some of the resolved component-spots. Development with ether/hexane and toluene/methanol mixtures (multi-development improves resolution somewhat), usually gives the best results. Visualisation is best attained by spraying with antim-ony trichloride in chloroform. In the context of clean-

up and elimination of some of the interfering polymer, the author has found that preliminary chromatography on a short micro-column, packed with silica, to be quite efficient. The latter can easily be constructed from a Pasteur disposable pipette. This depolymerisation procedure can further be reinforced by carrying out the chromatography on one of the commercial plates currently available, which employ a concentration-zone. Along the edge of the plate is a band of high pore diameter/medium pore volume silica, which is in intimate contact with a conventional silica-gel layer over the remaining area of the plate. The sample is applied to the concentration zone. Some of the polymer remains behind on the special layer, together with the more polar materials, whilst the bulk of the sample becomes concentrated into a small band at the interface of the two zones. Development is carried out in the normal manner.

Hptlc plates -high performance thin-layer plates- which employ finer particles of silica-gel within a much narrower size-range, certainly enhance sensitivity and resolution. Much shorter development distances are required and the spots are much less diffuse. However, a major drawback is that they are far more sensitive to polymer and polar contaminants. It is not a simple matter to apply a dilute solution and concentrate on the plate, which is often necessary with varnish samples. In general, application and technique is far more exacting and there is a strong tendency to overloading.

The National Gallery laboratory has applied the technique, but using two-dimensional development (ether/hexane (1) and methanol/toluene (2)), to one or two triterpenoid ambers, with moderate success. These, of course, represent an extreme of polymer and oligomer contamination and so are useful examples. However, once again, with complex mixtures or large amounts of drying-oil lipids present, the success rate for partial identification may be depressingly low. Nevertheless, it is a method which the reasonably competent chemist can try as a stop-gap method, should he lack access to more sophisticated techniques.

The main chromatographic method used in this laboratory is gas-liquid chromatography. Unless special methods such as pyrolysis gas chromatography are used, this form of analysis is insensitive, in certain respects to the polymeric material present. In theory, the chemist has two modes of approach when attempting to identify the resinous components of a varnish:

- 1). For those resins which have moderate amounts of polymer present or dry by linkage of polymerisable, monomer resin components, pyrolysis gas chromatography possibly offers the potential of a 'finger-printing' technique.
- 2). Trace amounts of monomeric indicator compounds, still persisting can be searched for.

Preliminary trials have been made on the first method, that is, the pyrolysis technique. At this stage it is difficult to assess the general applicability of this method, since the results reported were obtained

under severe limitations imposed by the particular pyrolysis equipment available for the study. The results reported below will be, in this instance, restricted to diterpenoid resin components only, for reasons to be explained.

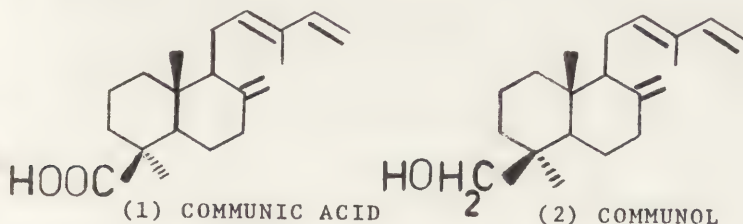
In each case the sample was allowed to stand overnight to remove, as thoroughly as possible, monomeric diterpenoid material. The swollen polymer was allowed to dry out and a small amount applied to a Curie-point pyrolysis wire. This had been filed, previously, to half the original diameter throughout the lower 10 mms., and then bent back upon itself. The fragment of polymer was trapped in the 'U'. Pyrolysis was carried out for 5 seconds at a nominal temperature of 770° C. Longer pyrolysis times were found to cause excessive fragmentation and so were avoided. The pyrolytic fragments were distributed on a 5 ft. x 1/4 inch column packed with 3% OV-1, pre-oxidised. The analysis was carried out with a temperature programme of 90°C., to 250°C., at a rate of 5°C. per minute. A bar-chart, below, summarises some of the results which were produced by the system. Nevertheless, it should be emphasised that there was variability within a common sample type and these results only represent a fairly typical run.

Factors which seemed to have a marked effect on the resultant pyrogram include sample size and the way in which it was applied to the pyrolysis wire, the pyrolysis temperature and how soon it was stabilised, whilst there was also a marked quantitative dependence on carrier gas-flowrate. However once these parameters had been standardised, the results were reasonably consistent qualitatively and to a certain extent quantitatively. Unfortunately, the equipment available did not permit the specification or standardisation of known key factors such as ramp-rate and rise time; in addition, no adequate preheat facility for the carrier gas was possible. Added to this, the arrangement of the pyrolyser head was such that it was not possible to ensure that the pyrolysis wire did not touch its silica sheath at various points. This in turn added local, pyrolysis temperature inhomogeneities by conduction and accounted for considerable loss in pyrolysis fragments by condensation on the surrounding walls. Indeed when triterpenoid resins were pyrolysed, very little was seen on the pyrogram and the amount of material deposited on the silica sheath of the pyrolysis tube was substantially greater. Only by putting the pyrolysis temperature up and increasing the pyrolysis time was the amount of condensate judged to be reduced. However, the resulting pyrogram showed low retention time fragments which were of little diagnostic value.

Nevertheless, despite the shortcomings of this limited study, with one of the more recent and flexible, on-column pyrolysis units (e.g. Ref. 3), permitting greater control of key parameters, many uncertainties would be removed with a marked improvement in reproducibility. Certainly the improved efficiency of transfer of pyrolysis products would result in more uniform sets of data. In particular, this technique when combined with wall-coat open tubular columns, provided with trap and reheat, should make a major step forward.
(Ref 4)

Broadly, four main polymer-class resins were chosen for trial studies. These were:-

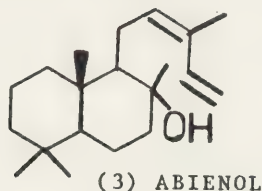
1).. A poly-communic acid skeletal type. Here the diene bi-cyclic, diterpenoid acids, cis- and trans-communic acids(1), originally present in the freshly bled resin, rapidly polymerise and thereby cause the resin to harden.



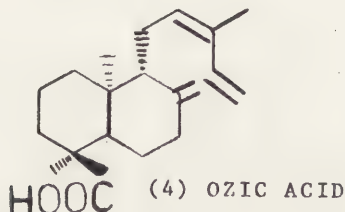
Low to medium molecular weight polymer of this type is found in the resin Tetraclinis articulata (Vahl) Masters and is probably the main source of the important resin known as sandarac.

2).. A copolymer of communic acid and the corresponding alcohol, communol.(2) The example included here comes from kauri resin, a semi-fossil product of Agathis australis Salisbury.

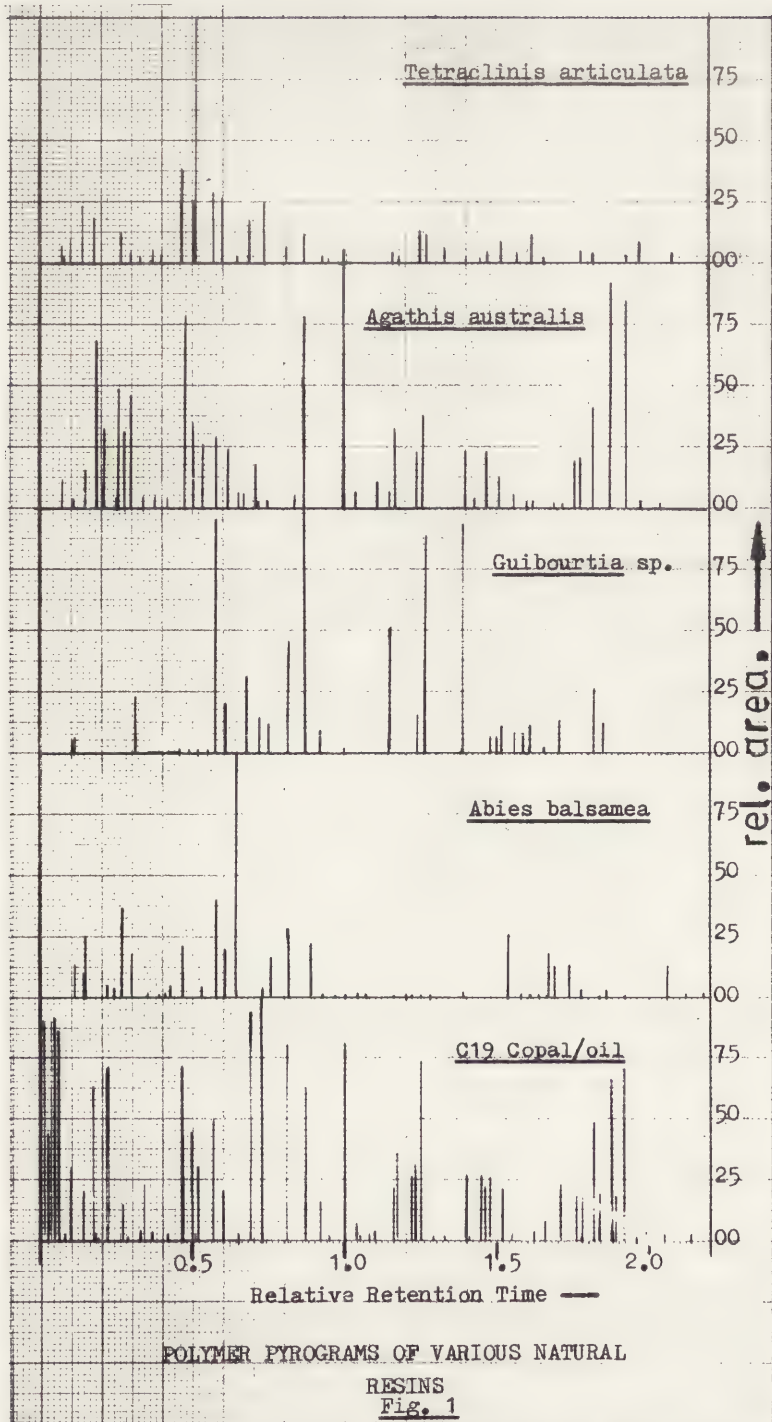
3).. A resin polymer based on abienol (3), common to the fir balsams. The example used below is from the resin of Abies balsamea (L) Mill.



4).. A polymer based on the monomer ozic acid (4). Here a sample of Congo copal was used (Guibourtia sp.).



5).. An example of an unknown copal/oil varnish film,



spread in the late 19th. Century.

The results are displayed in fig. 1.

In general, a somewhat higher analysis temperature for the gc column was used in an attempt to compress the lower retention time components, which accounted for the major part of the pyrolysis products, into an early envelope. The reason for this action was to try and exclude the more highly fragmented products and thus try to concentrate on the larger neutral fragments, which hopefully should be more indicative of the main structural types present in the polymer. In the instance of the copal/oil film, this early envelope was substantially greater than in the simple resin polymers examined above. This is presumably as a result of the ready breakdown of aliphatic chains in the oil to small fragments.

Much of the work carried out on varnish coatings in easel-paintings and museum objects at the National Gallery laboratory is based on the second of the two methods summarised above. A paper has already appeared outlining both the chemistry and the current literature available, on the natural resins. (Ref. 5) Examples of the analysis of varnish by gas chromatography are given therein. In addition, a more extended treatment of the analysis of instrument varnishes from the 18 th. Century was reported to the previous ICOM conference (Ref.6). Since that time the National Gallery Scientific Department has acquired the powerful technique of gas chromatography directly interfaced to a low resolution mass spectrometer, which in turn is coupled to a data system. This is currently helping to resolve some of the uncertainties encountered in varnish and medium analysis, particularly where complex resin mixtures are involved and in those cases where there are large amounts of soluble polymeric material and polar oxidation components. Here, unless the mixture can be adequately 'cleaned up', the analyst may well encounter unreliable retention data. This, in turn, reflects in a lack of certainty about the identity of key indicator compounds. Such uncertainties are considerably diminished when mass spectral data on that peak can be obtained, to characterise the component more fully and so supplement the approximate relative retention time.

Two key sets of information may be resolved by the use of low resolution gc-ms:-

1)... The molecular weight of a given component in the chromatogram.

2)... A molecular fragmentation pattern. This may help to 'finger-print' the compound through comparison with known, pure standard compounds or with compounds present in resins from a known botanical source. Alternatively, from theoretical considerations concerning bond-fracture during electron impact, it is possible to point to a partial or full chemical structure for the component under investigation. Certainly, when a data system is available, it is a considerable aid in analysis to simplify complex chromatograms by scanning for particular molecular

masses or mass-fragments. These chromatograms are known as mass chromatograms and enable the analyst to approach complexities of such mixtures in a more orderly and efficient manner. In some cases molecular mass chromatograms may be of aid, whilst in others a principle fragment chromatogram (or combination of principle fragments) can reveal those components of common skeletal type. Of course, most successfully of all, the analyst can build up for his particular system a library of fragmentograms (mass spectra) of compounds found in known resins and varnishes, both aged and fresh. Here, comparisons can be made by a suitable library search algorithm without the need for the analyst to elucidate the chemical structure. Two examples of the use of gc/ms will be discussed at the Conference, primarily intended to illustrate the scope and power of this technique. In one case, a relatively straightforward instrument varnish will be examined, whilst the other will be a more demanding, complex, picture varnish, containing components of widely varied skeletal types.

As well as combining the mass spectrometer with gas chromatography for analysis, some preliminary results have been published for direct characterisation of paint media using the direct-insertion, heated probe facility provided with most mass spectrometers. (Ref. 7)

Finally, a word of caution is offered concerning the use of gc/ms. Despite its power and potential, any laboratory considering possible venture into this field would do well to limit its attention to gas chromatography alone, at least until it has gained adequate analytical experience in paint media, natural adhesives and varnishes. Gc/ms can present formidable difficulties and without gc experience with samples from actual objects, as well as reference materials, these difficulties may prove insurmountable. It has certainly been the experience of the organic mass spectrometry unit at the National Gallery, that the use of high resolution capillary columns is far more satisfactory than packed columns. Here, special injection techniques, such as Grob splitless injection with cold trapping and solvent cutting are essential to give good chromatograms, column protection and to minimise source saturation and mass conversion disturbances.

REFERENCES.

- 1....KUHN, H., 'Detection and Identification of Waxes, Including Punic Wax, by Infrared Spectrography', Studies in Conservation, 5 (1960), 71-80.
- 2....WHITE, R., 'The Application of Gas-Chromatography to the Identification of Waxes', Studies in Conservation, 23 (1978), 57-68.
- 3....de WITT ROGERS, G., 'An Improved Pyrolytic Technique for the Quantitative Characterisation of the Media of Works of Art' in BROMMELLE & SMITH:

'Conservation and Restoration of Pictorial Art',Butterworths (1976), 93-100.

4.....JACQUES, C.A. & MORGAN, S.L., 'A Precolumn Cold Trap and Rapid ReInjection System for Pyrolysis Gas Chromatography with Capillary Columns', Journal of Chromatographic Science, 18 (1980), 679-683.

5.....MILLS, J.S. & WHITE, R., 'Natural Resins of Art and Archaeology. Their Sources, Chemistry and Identification', Studies in Conservation, 22 (1977), 12-31.

6.....WHITE, R., 'An Examination of Varnish from Three Eighteenth Century Musical Instruments', ICOM Committee for Conservation, Zagreb (1978), 78/16/1.

7.....WEISS, N.R. & BIEMANN, K., 'Application of Mass Spectrometric Tecchniques to the Identification of Paint Media' in BROMMELLE & SMITH: 'Conservation and Restoration of Pictorial Art', Butterworths (1976), 88-92.

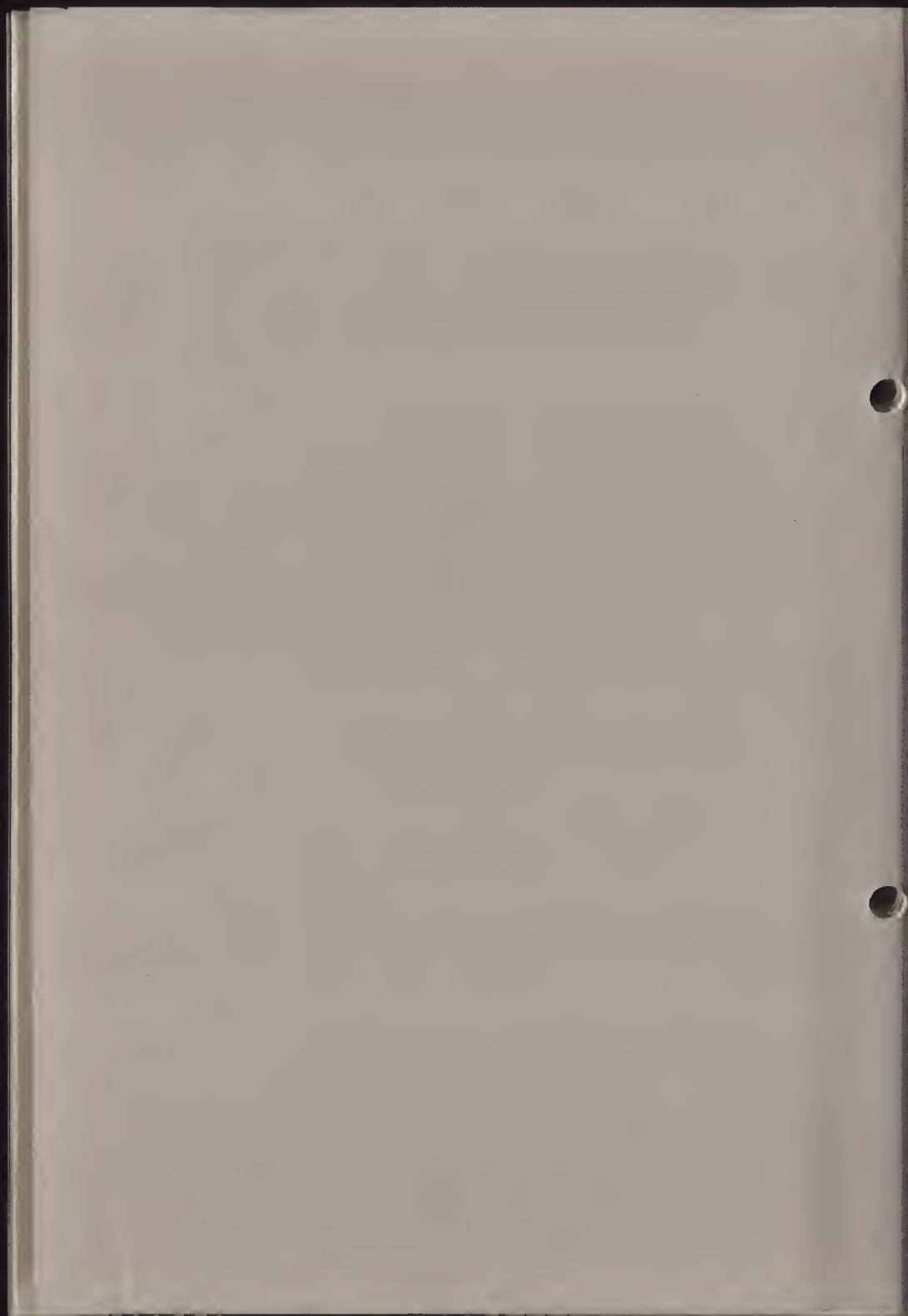
81/16/3

CONTRIBUTION TO THE STUDY OF NATURAL RESINS
IN THE ART

L. Masschelein-Kleiner and P. Taets

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Protective Coatings,
Traditional and Modern



CONTRIBUTION TO THE STUDY OF NATURAL RESINS IN THE ART

L. Masschelein-Kleiner and P. Taets

Institut Royal du Patrimoine Artistique
1 Parc du Cinquanteenaire
1040 Bruxelles
Belgium

RESUME

A general method of analysis is proposed for natural resins. It enables also the detection of oils, waxes and paraffin, and the identification of resins.

INTRODUCTION

The study of natural resins is an old tradition in our laboratory[1,2,3]. Numerous works have been made already in this field[4,5,6,7] but, as MILLS and WHITE pointed it out in their exhaustive review[8], this class of material is very difficult to analyze.

Terpenes are produced by numerous trees all over the world. Each resin is a complex mixture of many constituents which are often not entirely identified and which are very sensitive to ageing.

Recent advances have been made during the last few years[9,10,11] which enables us to characterize natural resins in a series of old varnishes and resins.

EXPERIMENTAL

Methyl ester formation

5mg of resin are placed in a frozen tube with 0.2ml

of sodium methoxide[N] in methanol. The tube is sealed and placed in an oven at 100°C for 45 min. [9]. Esterification is indicated by the complete solution of the sample. This is not the case with hard copal such as Kauri of Madagascar copals.

The tube is then opened and 0.2 ml sulfuric acid (10% in methanol) is added. The tube is sealed again and placed in an oven at 135°C for 45 min. [10]. After cooling, the tube is opened, the methyl esters are extracted with 2 ml of chloroform and washed twice with water. The solution is evaporated to about 0.1 ml.

Gas chromatography

The instrument is a Hewlett-Packard 5750G, dual column temperature programmed gas chromatograph. The columns are 225 cm long, 2 mm in diam., glass packed with 3% SP2250 on Supelcoport 100/120 mesh. Helium flow rate is 60 ml/min. with temperature programming at the rate of 4°C/min from 100°C to 290°C. After reaching this temperature, the latest is held constant until the complete elution of all the components. The diterpenoid fractions are eluted between 15 and 40 min., the triterpenoid fractions between 40 and 60 min after the injection.

Thin-layer chromatography

Precoated plates of silicagel with concentrating zones are used (Merck 60F254; n°11798). The thickness of the layer is 0.25 mm and the concentrating zone is 2.5 cm long.

The eluant is a mixture benzene+methanol (92:8).

The spray reagent, Vanadium pentoxide is prepared according to [11]:

1.62 g of anhydrous ammonium metavanadate is dissolved in 125 ml concentrated sulfuric acid at 150°C. After cooling it is added to 125 ml of ice-cold water giving a deep orange solution. The spray reagent is obtained by diluting this solution ten times.

After spraying, the eluted plates are placed in an oven at 110°C for 2 min. They are then observed under U.V. light.

RESULTS AND DISCUSSION

Analysis of varnishes

Saint Roch, XVIth century, Saint Martin church, Toghogne (Belgium), polychromed sculpture.

The varnish was taken off from the surface of a layer dated from the XVIIth century. The first sample comes from

Child's face, the second one from the body of the boy.
The varnish is gold-yellow and very fragmentary.

The chromatograms obtained after methylation are the same for both samples. They are typical of a pine resin [6] and more particularly of Bordeaux turpentine (*Pinus maritima*) [12], (figures 1 A and B).

The identification of Bordeaux turpentine is confirmed by thin-layer chromatography.

Fragment of an Antwerps retabel, XVIth century, Musées Royaux d'Art et d'Histoire, Brussels, polychromed sculpture.

The varnish was found on the original layer. Here again we find the components of Bordeaux turpentine. Additional peaks on the gas chromatogram indicate the presence of a little oil, (figure 1 C). Paraffin which was probably used as a fixative in a previous treatment, is also clearly visible (figure 1 D).

Thin-layer chromatography shows the presence of Bordeaux turpentine.

The "Holy Kinship", after J. van Coninxlo, XVIth century, Steenokkerzeel's church (Belgium), painting on panel.

The varnish was dark brown but remained fairly soluble. It contains a good deal of oil, Bordeaux turpentine and turpentine (figure 2 B).

The nature of the resin is confirmed by thin-layer chromatography.

The "Descent from the Cross", P.P. Rubens, XVIIth century, Antwerp's Cathedral, painting on panel.

This modern varnish was taken off from the left panel. It dates probably from the last intervention (in 1946) before the treatment of the painting at the Institute. KLEBER and TRICOT-MARCKX had already investigated it and they identified mastic resin by means of thin-layer chromatography [13].

The gas chromatogram confirms the presence of mastic, together with oil and turpentine (figure 2 C). Traces of pine resin are quite probable.

Analysis of resins

Saint Christopher, end of the XVth century, Brussels school, Private collection, polychromed sculpture.

The sample comes from the green glaze of the grass which was painted on the base.

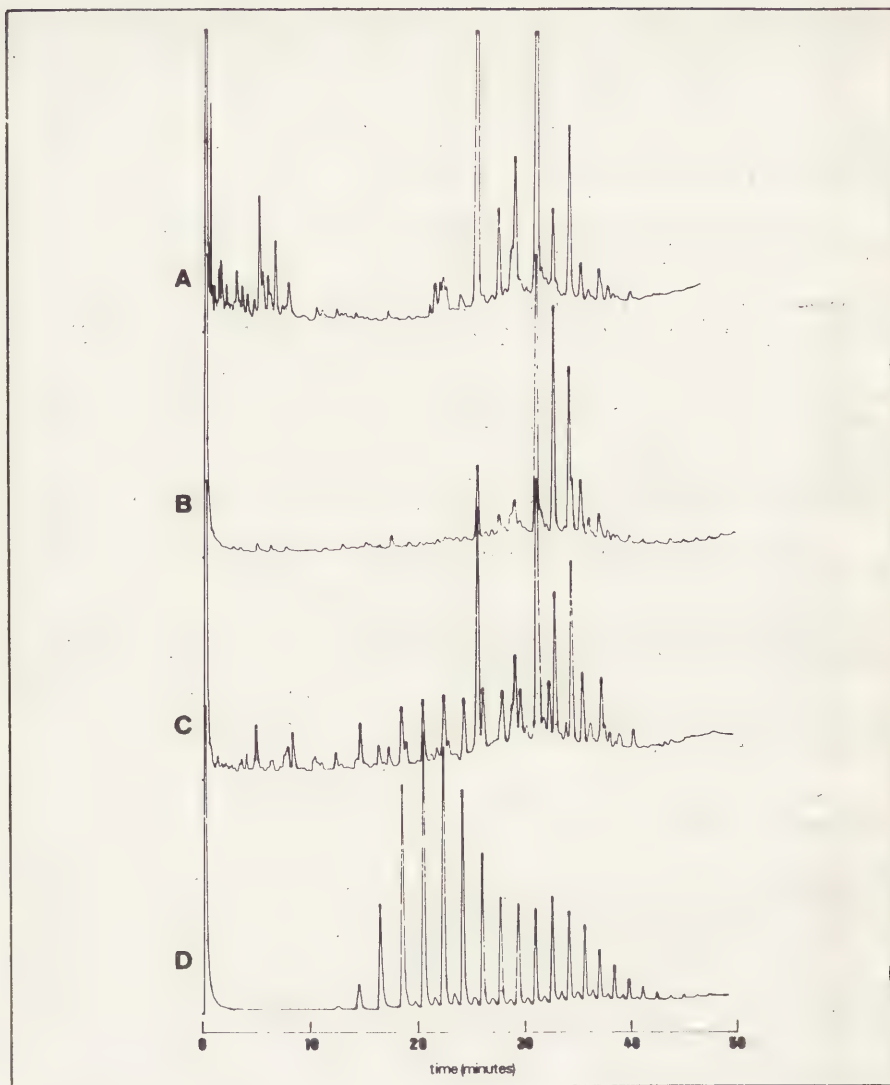


FIGURE 1: [A] Bordeaux turpentine (*Pinus maritima*); [B] St Roch, polychromed sculpture, St Martin's church, Tohogne (Belgium): the varnish dates probably from the XVIIth century; [C] Fragment of an Antwerps retabel, XVIth century, Musées Royaux d'Art et d'Histoire, Brussels [D] Paraffin wax.

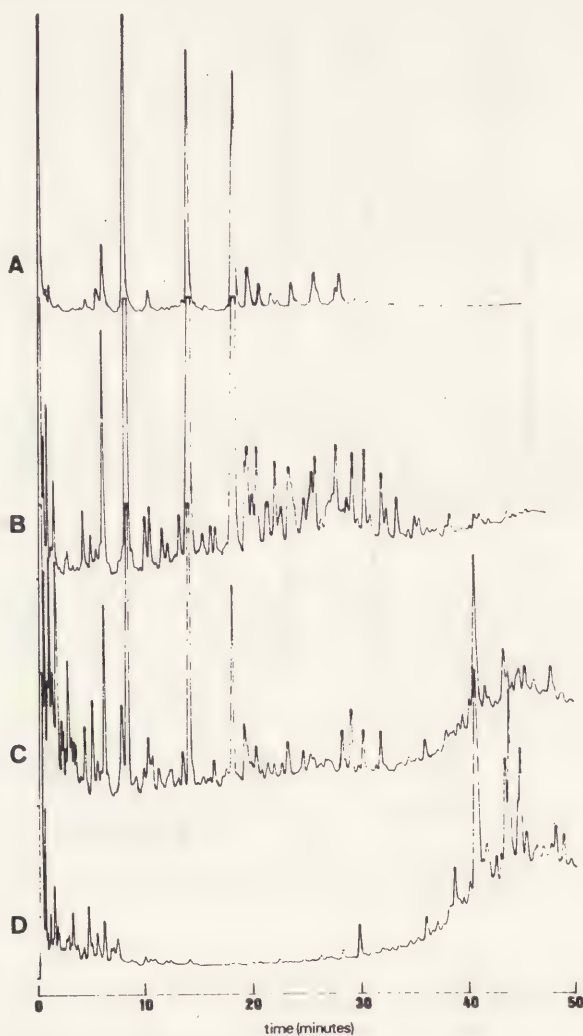


FIGURE 2: [A] Aged linseed oil; [B] "The Holy Kinship", after J. van Coninxlo, XVIth century, Steenokkerzeel, (Belgium); [C] "The Descent from the Cross", P.P. Rubens, XVIIth century, Antwerps' Cathedral; [D] Mastic resin (*Pistacia lentiscus*).

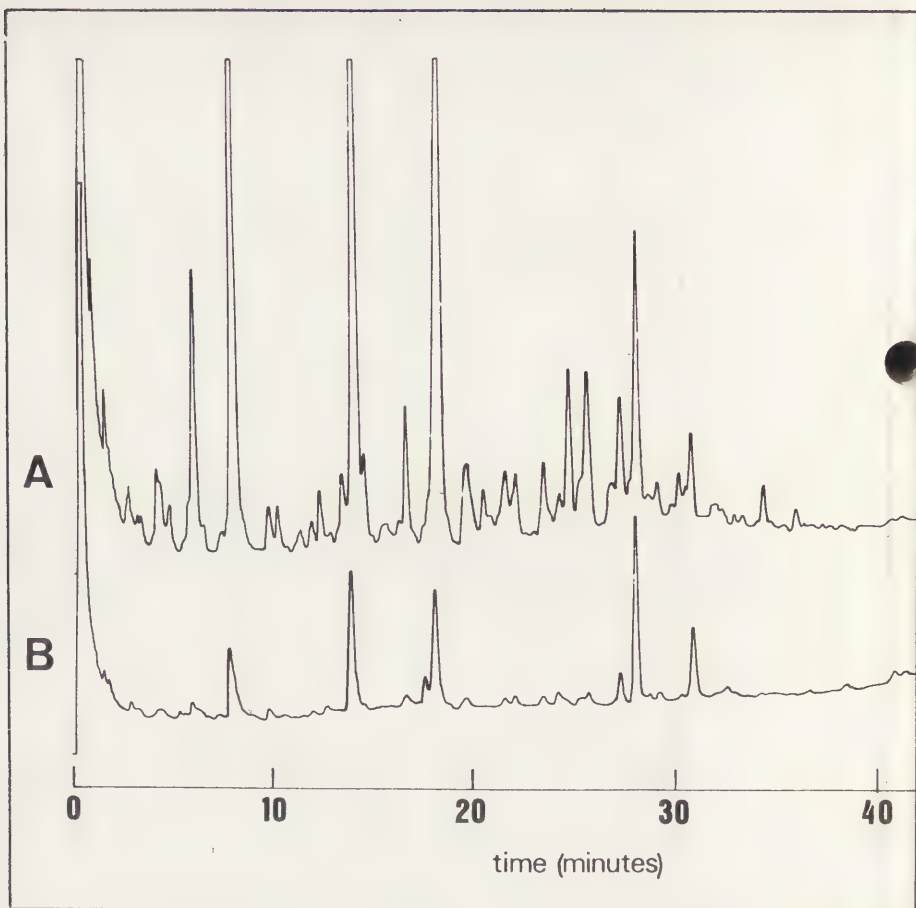


FIGURE 3: [A] St Christophe, polychromed sculpture, Brussels school, end of XVth century, private collection: green glaze on the grass; [B] Calvary, Albert Bouts, XVth century, Musées Royaux des Beaux-Arts, Brussels: brown glaze.

We find oil as the main component: this is probably the binding medium. The resin is of the pine family, probably *Pinus sylvestris*, (figure 3 A).

The microprobe indicates that copper is present in large amounts. This green glaze seems thus to be made of the copper salt of a pine resin.

Traces of wax from a fixative are also detected.

Calvary, Albert Bouts, XVth century, Musée Royal des Beaux-Arts, Brussels, painting on panel.

The sample was taken from a brown glaze in the landscape. We identify oil and a pine resin. This sample is closely similar to the previous one (figure 3 B).

However copper is present only as traces and we did not find any other metal which could promote the color. The latest was perhaps achieved by addition of a brown dyestuff.

CONCLUSION

Pine resins seem to have been of very frequent use in our country since the Middle Ages and probably sooner. They were certainly, just like now, easy to find and cheap. Moreover their acidity is an advantage for the formation of resinates.

ACKNOWLEDGMENT

We thank Mr. L. Maes, industrial engineer for the analysis by microprobe.

BIBLIOGRAPHY

- [1] L. MASSCHELEIN-KLEINER, "Perspectives de la chimie des liants picturaux anciens", Bulletin I.R.P.A., VI (1963) 109-126.
- [2] R. KLEBER and L. MASSCHELEIN-KLEINER, "Contribution à l'analyse des composés résineux utilisés dans l'art". Bulletin I.R.P.A., VII (1964) 196-218.
- [3] L. MASSCHELEIN-KLEINER, J. HEYLEN and F. TRICOT-MARCKX, "Contribution à l'analyse des liants, adhésifs et vernis anciens", Studies in Conservation, 13 (1968) 105-121.
- [4] R. L. FELLER, "Special report on identification and analysis of resins and spirit varnishes", Mellon Institute.

[sept.1958].

[5]R.L.FELLER,"Dammar and mastic I.R.analysis",Science,
120(1954)1069-1070.

[6]J.S.MILLS and A.E.A.WERNER,"Paper chromatography of
natural resins",Nature,16(1952)1064-1070.

[7]J.S.MILLS and A.E.A.WERNER,"Partition chromatography
of natural resins",J.Oil and Colour Chem.Assoc.,37(1954)
131-142.

[8]J.S.MILLS and R.WHITE,"Natural resins of art and
archaeology, Their sources, chemistry and identification",
Studies in Conservation,22(1977)12-31.

[9]J.M. de MAN,"A comparison of three methods of methyl
ester formation for the gas chromatographic analysis of
Fatty acid composition of natural fats",Laboratori
Practice,16(1967)150-153.

[10]A.PIETTE and I.SUYS,Laboratoire Intercommunal de
Chimie et de Bactériologie,Brussels:private communica-
tion.

[11]M.MALALYANDI,J.P.BARETTE and M.LANOUTTE,"Vanadium
pentoxide as a chromogenic spray reagent for the
qualitative analysis of some organic compounds on thin-
layer plates",J.of Chromatography,101(1974)155-162.

[12]T.H.BARRY,"Natural varnish resins",E.Benn -London
(1932).

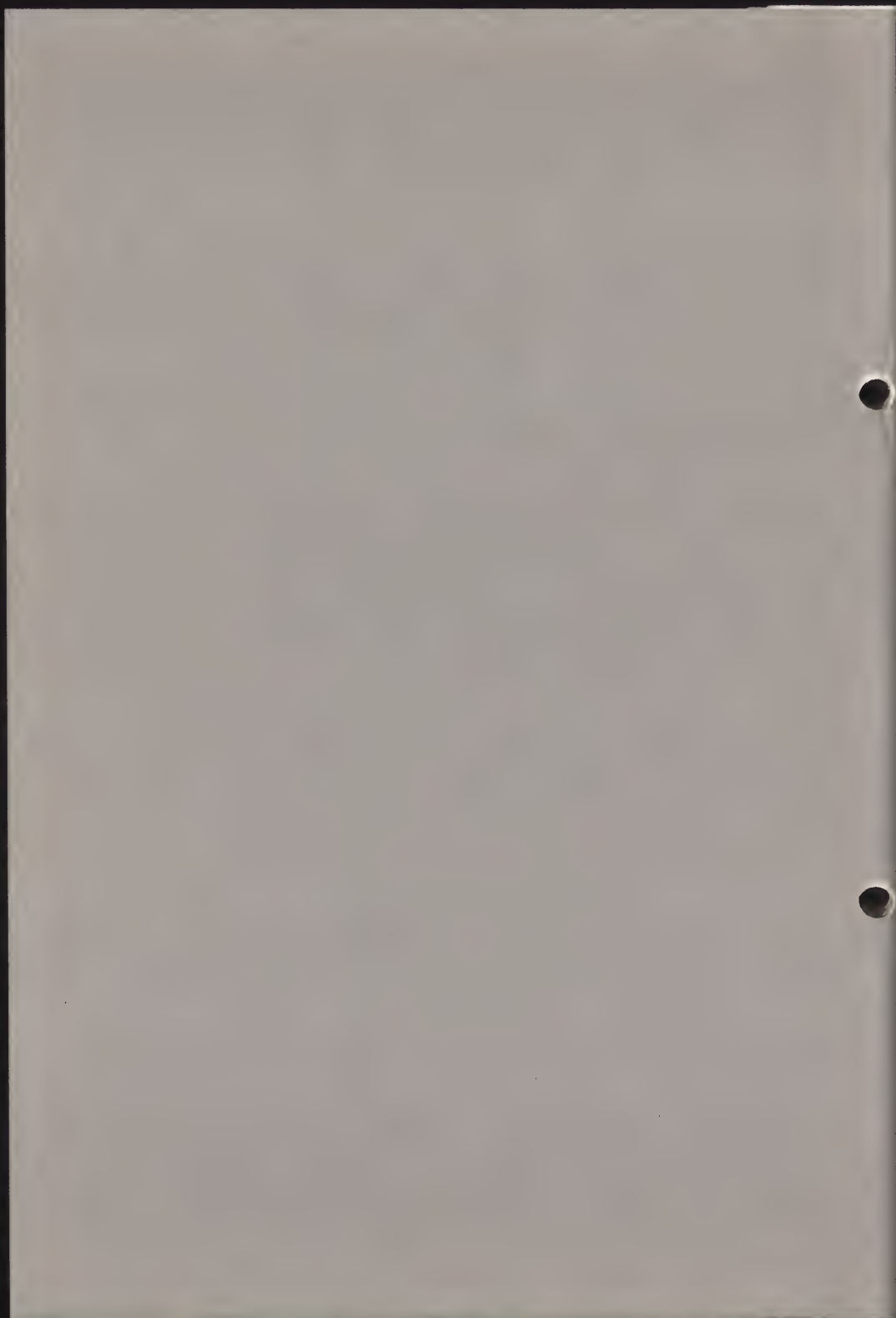
[13]R.KLEBER et F.TRICOT-MARCKX,"Identification d'un
vernis moderne recouvrant la "Descente de Croix" de
P.P.Rubens",Bulletin I.R.P.A.,VI(1963)63.

SYNTHESIS OF AN ACRYLIC VARNISH WITH HIGH
REFRACTIVE INDEX

E. De Witte, M. Goessens-Landrie, E.J.Goethals,
K. Van Lerberghe and C. Van Springel

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Protective Coatings,
Traditional and Modern



SYNTHESIS OF AN ACRYLIC VARNISH WITH HIGH REFRACTIVE INDEX

E. De Witte, M. Goessens-Landrie, E.J.Goethals,

K. Van Lerberghe and C. Van Springel

E. De Witte and M. Goessens-Landrie
Koninklijk Instituut voor het Kunstpatrimonium
Jubelpark 1
1040 Brussels
Belgium

E.J.Goethals
Rijksuniversiteit Gent
Laboratorium voor Organische Chemie
Gebouw S4
Krijgslaan 271
9000 Ghent
Belgium

K. Van Lerberghe and C. Van Springel
Universiteit Antwerpen-RUCA, Lab. Chemische Technologie HI
Schildersstraat 41
2000 Antwerp
Belgium

ABSTRACT

The influence of refractive index and viscosity grade on the colour rendering effect of picture varnishes is investigated. The results lead to the synthesis of an acrylic copolymer of phenyl acrylate and methyl methacrylate (30/70) with a high refractive index and a low viscosity grade. The physical properties and the ageing behaviour indicate that it is worthwhile to consider the resin as a promising base for a new picture varnish, although further research is still necessary.

1. Introduction

The final stage of the restoration of a painting consists in the application of a varnish coat on the paint layer. The purpose of this layer is threefold:

- to protect the paint layer against slight mechanical damages
- to allow a regular, superficial cleaning (removal of dust) without damaging the paint layer
- to bring the colours to their exact chromatic value

Although the restorer presently disposes over a large scale of commercial varnishes, the perfect protective coating for paintings is not yet available. The resins used as picture varnishes can roughly be subdivided into two classes:

- varnishes with excellent optical properties but poor chemical stability (damar, polycyclohexanones)

- varnishes with moderate optical properties and excellent chemical stability (Paraloid B 72, polyvinyl acetates)

The ideal varnish should of course combine the excellent optical properties with a good chemical stability. The latter is mainly determined by the chemical structure of the resin. Extensive work by Feller (1) shows that acrylics have a far better stability than the other resins. Paraloid B 72 is even proposed as reference material for resins of class A (2). As the restorers of our Institute judge the optical properties of Paraloid B 72 insufficient for varnishing old flemish paintings, presently, a combination of two varnish coats is applicated. The painting is varnished, at first, with a thin coat of polycyclohexanone resin (Keton N) and after drying, a coat of Paraloid B 72 is applied on top of it. This system gives the colours an acceptable chromatic value, has the advantage that the upper varnish layer resists gentle cleaning and is free of blooming. Unfortunately, the degradation of the polycyclohexanone may interfere with the stability of the acrylic resin (3).

The purpose of the present work was to develop a material which combines the chemical stability of the acrylics with the colour rendering of damar or Keton N. The chemical stability was achieved by using acrylic esters as starting material. According to Feller (4) the colour rendering is in the first place influenced by the viscosity grade, although the refractive index of the material probably also plays an important role. Therefore, an investigation was included to find out the influence of refractive index and viscosity grade on the appearance of varnishes.

2. Colour rendering of varnishes.

The appearance of multiple reflections in a varnish coat makes the colours look more saturated (5). This increase in saturation is said to be easily observed by an experienced restorer, but certainly is difficult to detect by an instrumental measurement. It therefore was tried out whether or not a visual appreciation by restorers may be considered as sufficiently reliable. Several varnishes, or varnish systems, were applied on different areas of 18th and 19th century paintings. As it was found that large differences in gloss can influence the judgement, the varnishes were gun sprayed in such a way that all of them had a gloss of the same

order of magnitude. Then the painting restorers of the Institute were asked to judge, individually, the varnishes and to list them in decreasing order of colour rendering. The restorers were not informed about the nature of the varnishes and several applications of the same varnish could detect the reliability of each individual restorer. The results of the reliable judgements in table 1 show that damar is found to give the best results, followed by Keton resin N and Paraloid B 72. The colour rendering of the varnish systems, Paraloid B 72 on top of Keton N or Keton N on top of Paraloid B 72, is determined by the underlaying coat.

Table 1: Classification of the colour rendering of different varnishes by the restorers of the Institute.

Varnish	Classification	Refractive index	Visc.grade
Damar	1	1.53	
Keton resin N	2	1.515	1.2
Keton N/B 72	2	1.517/1.482	1.2/43.7
Paraloid B 72	3	1.482	43.7
B 72 / Keton N	3	1.482/1.517	43.7/1.2

The tests showed also that it is harder to make a classification on light colours than on dark ones, but in all cases the results are identical.

3. Influence of refractive index and viscosity grade on the colour rendering.

In order to find out which is the more important factor in colour rendering, either the refractive index or the viscosity grade, two series of polymers were prepared:

- a series with constant viscosity grade and varying refractive index
- a series with constant refractive index and varying viscosity grade

3.1. Influence of refractive index

Groat (6) described a method to obtain polymers with any refractive index in the range of 1.477 to 1.550 by copolymerization of isobutyl methacrylate and styrene.

A series of copolymers was prepared and the reactions were carried out in such a way that the viscosity grade of all polymers was of the same order of magnitude. The refractive index was measured by applying a solution of the resin in acetone on the prism of an Abbe refractometer. After evaporation of the solvent at 60°C., the exact refractive index can be read. Four resins were applied on several oil paintings in the same way as described before. The restorers again made a classification of decreasing order of colour rendering. The results are summarized in table 2. As can be seen, the resins with higher refractive index give better results than these with lower ones.

3.2. Influence of viscosity grade.

Several polymers with the same refractive index but with a range of viscosity grades from 6.4 to 66.4 cps were prepared by copolymerization isobutyl methacrylate and styrene using different initiator concentrations. The viscosity grade, as defined by Feller (1) was measured with a Höppler viscosimeter. From the results in table 2 it can be concluded that the quality increases with decreasing viscosity.

Table 2: Influence of refractive index and viscosity grade on colour rendering.

Refractive index	Viscosity grade	Classification
1.55	18.6	1
1.53	17.0	2
1.50	14.2	3
1.47	13.0	4
1.505	6.4	1
1.505	14.2	2
1.506	66.4	3

4. Synthesis of acrylics with high refractive index.

The above mentioned experiments show clearly that the ideal varnish should have a high refractive index and a low viscosity grade. The compounds prepared in previous experiments could not be used as a styrene containing polymer is known to have a poor light stability.

The problem was to synthesize an acrylic varnish with a high refractive index. The refractive index can be increased by incorporation of aromatic nuclei. Therefore, a series of polymers containing aromatic nuclei such as polyphenyl acrylate, polybenzyl acrylate and polybenzyl methacrylate was prepared. Also copolymers with methyl methacrylate were synthesized.

A preliminary investigation on film forming properties and stability showed that the best results could be expected with a phenyl acrylate / methyl methacrylate (PHA/MMA) copolymer. The refractive index of a 30/70 copolymer is 1.547. Colour rendering tests, comparing this resin with damar, Keton N and Paraloid B 72 showed that the optical properties are better than these of Keton N and Paraloid B 72 and at least comparable with damar.

4.1. Stability.

The ageing of the PHA/MMA copolymer was compared with that of Paraloid B 72. A set of blue wool cloths were set along with the resins in the ageing apparatus, a XENO LEP 6000 xenon-arc fadeometer. Under the exposure conditions blue cloth N° 6 was noticeably faded after 140 h. The test was continued for another 140 h and even after this period, no visual changes such as yellowing, cracking or blistering could be noticed. Solubility tests with the solvent mixtures proposed by Feller (2) showed that before ageing, Paraloid B 72 is slightly better soluble than PHA/MMA. After ageing the solubility of PHA/MMA increases. This can be caused by chain degradation. A scratch test after Clemens (B.N.: DEF 1053 meth. 24) gives similar results for both resins: the first scratches appear with a load of 200 g, the knife cuts straight through the films with a load of 800 g. The stress - strain curve and the results of a König Swinging Beam are also comparable for both resins. These results indicate that the PHA/MMA copolymer can be classified in class A of the Feller classification. Presently, the behaviour of the new material on paintings is investigated. If the results are satisfactory, the last problem to be solved is the scaling up of the synthesis.

Table 3: Solubility of Paraloid B 72 and PHA/MMA copolymer.

Mixture	B 72		PHA/MMA	
	not aged	aged	not aged	aged
cyclohexane/toluene	75/25	50/50	25/75	75/25

5. Conclusion.

The visual evaluation of several polymers applied as varnishes on old oil paintings allow to conclude that the refractive index as well as the viscosity grade are important for the colour rendering.

The refractive index should be as high as possible, the viscosity grade rather low.

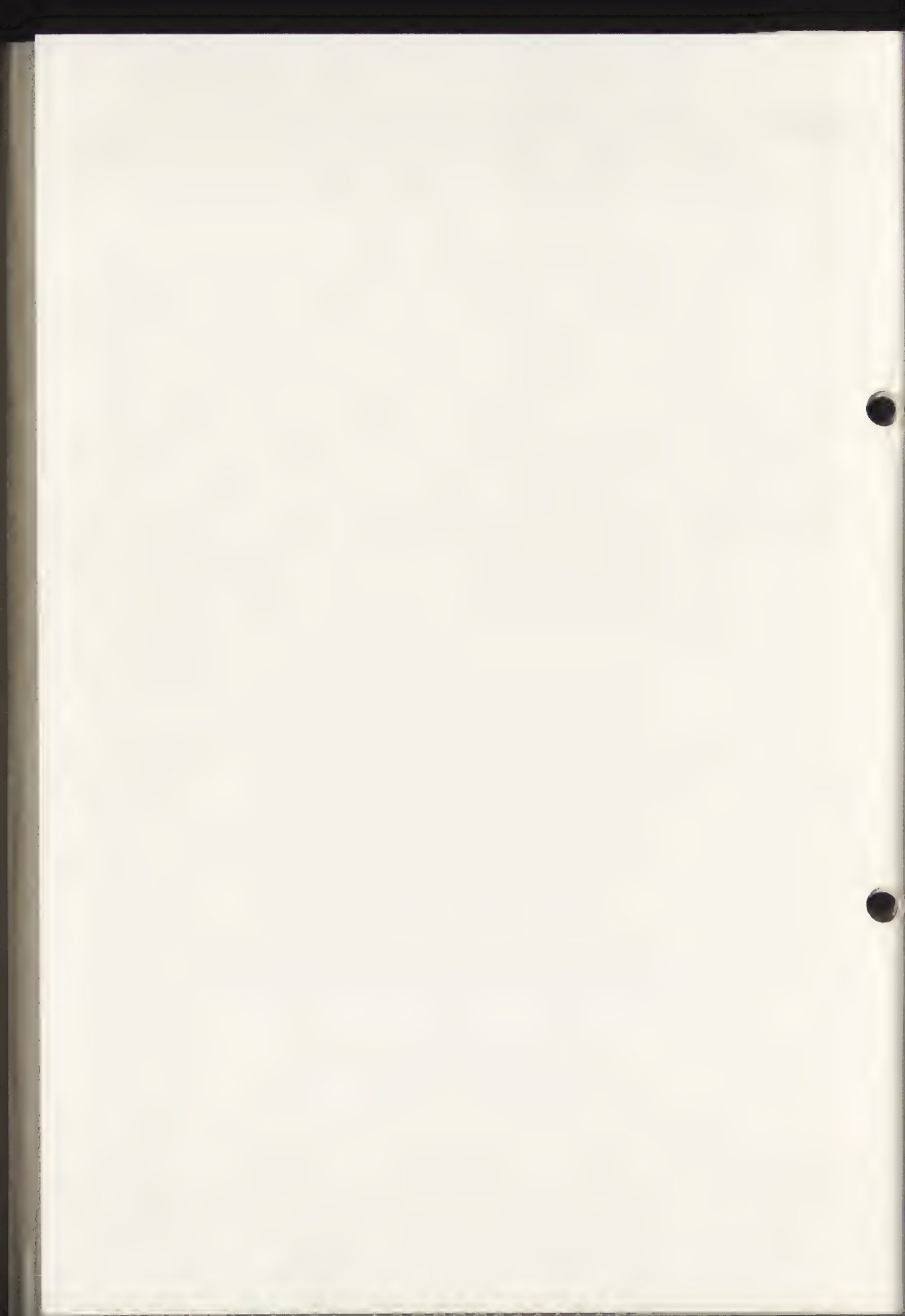
From a series of synthesized polymers a copolymer of phenyl acrylate/ and methyl methacrylate (30/70) gave the most promizing results. The physical properties of this material are comparable with those of Paraloid B 72. The ageing tests show that the new resin can be classified in class A and that the optical properties are at least as good as those of damar.

Further investigation of the stability on paintings is still necessary before the polymer can definitively be proposed as new picture varnish.

Acknowledgement: the authors thank the NFWO (Nationaal Fonds voor Wetenschappelijk onderzoek) for the financial support of the project and the painting restorers of the Koninklijk Instituut voor het Kunstpatrimonium for their usefull collaboration.

LITERATURE

1. R.L. Feller, N. Stolow, E.H. Jones. On picture Varnishes and their Solvents. The Press of Case Western Reserve University, Cleveland, 1971
2. R.L. Feller. Standards in the evaluation of thermoplastic resins. ICOM Committee for Conservation. 5th Triennial Meeting, Zagreb, 1978. 78/16/4
3. E. De Witte, in preparation
4. R.L. Feller. Factors affecting the appearance of picture varnishes. Science, 125 (1957) 1143-1144
5. E. De Witte. Surface Coatings for Modern Paintings. International Symposium on the Conservation of Contemporary Art, Ottawa, 1980
6. R.A. Groat. Preparation of copolymers of isobutyl methacrylate and styrene for mounting media. Stain Technology, 25 (2), 1950, 87-94.



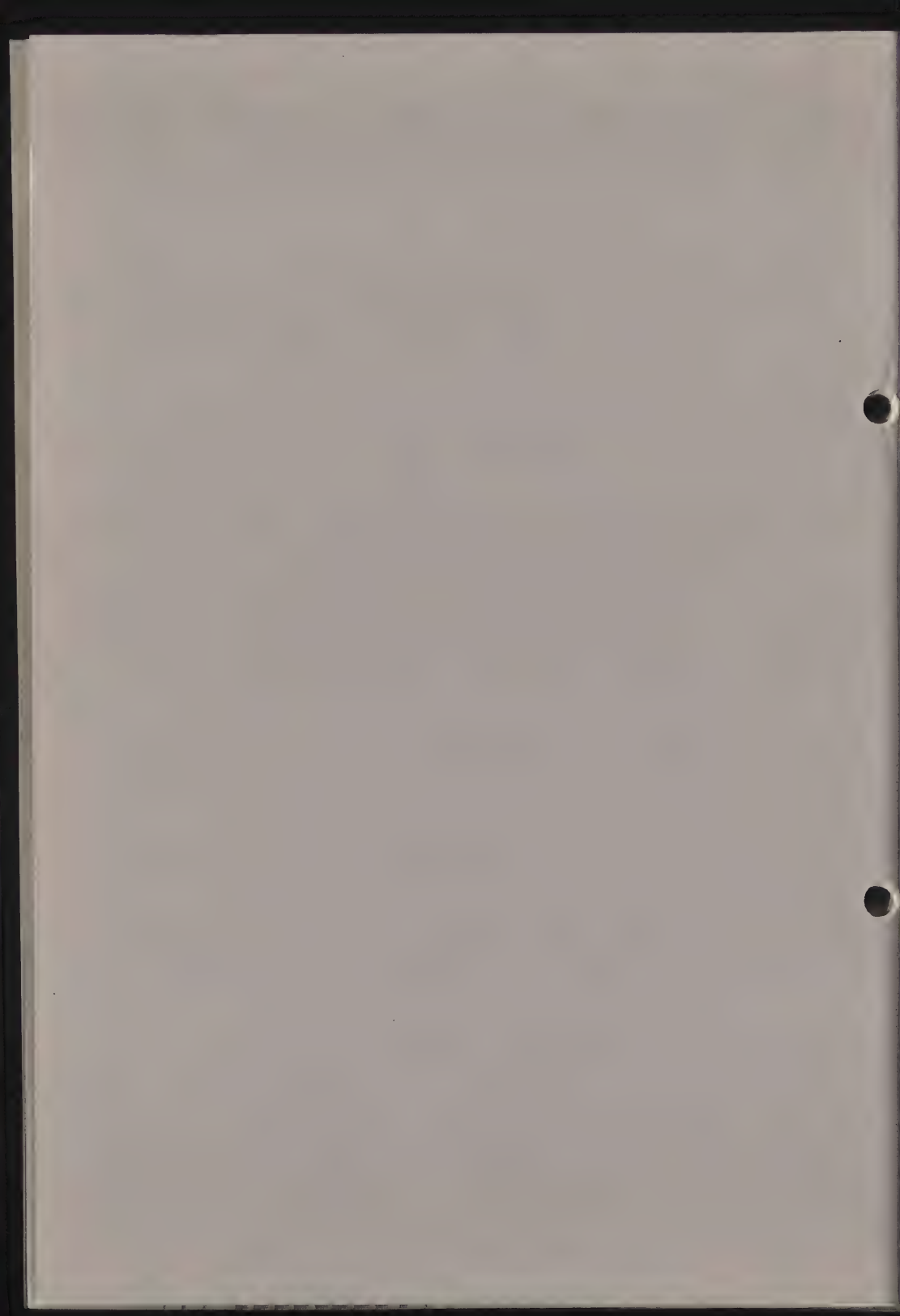
81/16/5

USE OF STABILIZERS IN VARNISH FORMULATIONS

Raymond H. Lafontaine

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Protective Coatings,
Traditional and Modern



USE OF STABILIZERS IN VARNISH FORMULATIONS

Raymond H. Lafontaine

Environment and Deterioration Research Division
Canadian Conservation Institute
1030 Innes Road
Ottawa, Ontario K1A 0M8
Canada

Abstract

Research done at the Canadian Conservation Institute on the use of stabilizers in varnish formulations is summarized. The yellowing of dammar varnish can be effectively reduced with certain antioxidants, in particular Irganox 565. Similarly, changes in solubility of Ketone Resin N due to photo-oxidation and crosslinking is slowed down by the incorporation of suitable uv absorbers and antioxidants. The need for a sound, rational approach to accelerated ageing techniques is discussed in light of the end-use of the materials tested. The methods used in some recent work on epoxy adhesives in the author's laboratory is summarized.

Introduction:

Most plastic materials consist essentially of a synthetic polymer base to which some kind of additive has been added. Even today, with an almost endless list of polymers, very few plastics are formulated without at least one additive to improve or change some property. It is not uncommon to have more than one additive in a given polymer system.

Polyvinyl chloride (PVC), for example, would not be a commercially viable polymer were it not for additives. A heat stabilizer is essential to all PVC formulations to prevent thermal degradation during processing. The list of additives used in plastics includes lubricants, processing aids, impact modifiers, plasticizers, biocides, emulsifiers, foaming agents, fillers, antistatic agents, flame retardants, antioxidants and UV stabilizers.

Additives have one thing in common. They improve, enhance or change some property of the polymer. A plasticizer, for example, is used to reduce the brittleness of the plastic and increase its flexibility. Without plasticizers many

plastics would just break or shatter under impact. Thus, the plasticizer is as important to the final formulation as the polymer itself.

In the field of conservation, additives are also used in resin formulations, but to a lesser extent. For example, a small quantity of wax might be added to a Ketone Resin N solution to reduce the brittleness and gloss of the final coating. Matting agents are also used in many varnish formulations.

Perhaps the most important additives are those that increase the useful life-span of a polymer. This category would include such compounds as antioxidants, thermal stabilizers and uv absorbers. Durability, stability, weatherability, all these terms take on a different proportion in the field of art conservation. To the plastic and paint industry long lasting might signify ten years. In conservation, 50, 100 years, even longer are commonly considered to be acceptable standards of stability. It is inconceivable that stabilizers cannot and should not play a bigger role in many varnish formulations.

This laboratory has in the past several years made some important contributions in the field of stabilization using antioxidants and UV absorbers. This work has led to improved coatings in the field of fine art. Prior to these studies, the application of stabilizers in varnish formulations for conservation had been limited. [1]

The use of antioxidants in Dammar varnish.

Dammar resin has been used extensively as a varnish for paintings until, in the mid-twentieth century the more durable synthetic resins became more popular. The changeover to synthetic resins was dictated primarily by the need to give priority to the preservation and well being of paintings. Most natural resins deteriorate rather rapidly. In the case of dammar, a tendency to yellow and darken with time is its major disadvantage. It is believed by many, however, that no other resin can bring out the full depth and transparency of colours so well as a freshly applied film of dammar. Since frequent cleaning and varnish removal is a potential cause of harm to a painting, the more durable synthetic resins have been adopted, and now dammar is very rarely used in modern restoration studios.

Studies done at the Canadian Conservation Institute resulted in the development of a dammar formulation whose rate of yellowing has been reduced considerably. Since yellowing of dammar is most likely a free-radical oxidation process, it

was correctly assumed that the addition of a suitable antioxidant would effectively reduce yellowing rates.

For test purposes it was found necessary to accelerate in some way the relatively slow process of yellowing. Exposure of the varnish samples to elevated temperatures (100°C) produced satisfactory results, visible yellowing being achieved in a few days instead of several years. By repeating the ageing at 50°C and also at room temperature, the relationship between normal gallery conditions and accelerated ageing could be estimated.

In order to facilitate the comparison of the degree of yellowing from one film to another, a 'yellowness index' was defined to be the change in percentage transmittance at 380 nm. This value, which could be read directly from the %T curves, proved very useful for plotting graphs of yellowing vs. time.

About 20 different antioxidants were evaluated as to their effectiveness in reducing dammar's rate of yellowing. Table 1 lists these antioxidants and the resulting yellowing at various intervals of ageing for films prepared with a 20% dammar in toluene and 1% wt/wt of resin of that particular compound. It was found that Irganox 565 was the most effective antioxidant. (Some 10 compounds were immediately discarded because they produced highly coloured solutions.) Certain antioxidants actually increased the rate of yellowing (F, G, J, M, O, P).

Figure 1 shows a plot of yellowness index vs. time at 100°C for the three most interesting cases. There is no doubt that when oil of turpentine is used as solvent, the resulting films yellow more rapidly than those prepared with toluene. Also, the addition of Irganox 565 reduces significantly the rate of yellowing.

On the average, a change in %T at 380 nm of less than 15 was found acceptable to most conservators, assuming that this yellowing occurred over a time span of 100 years.

Visually, a film with a yellowness index of 15 was only very slightly yellow. A change represented by an index of about 6 or less could not be perceived by the human eye, which is not as sensitive as the instrumentation used to measure the change. Even indices of 20 to 25 might be tolerable in many cases. Any yellowing above 25 was considered too pronounced and was immediately rejected. As a rule of thumb, a limit of 20 was chosen as the borderline between acceptable and unacceptable.

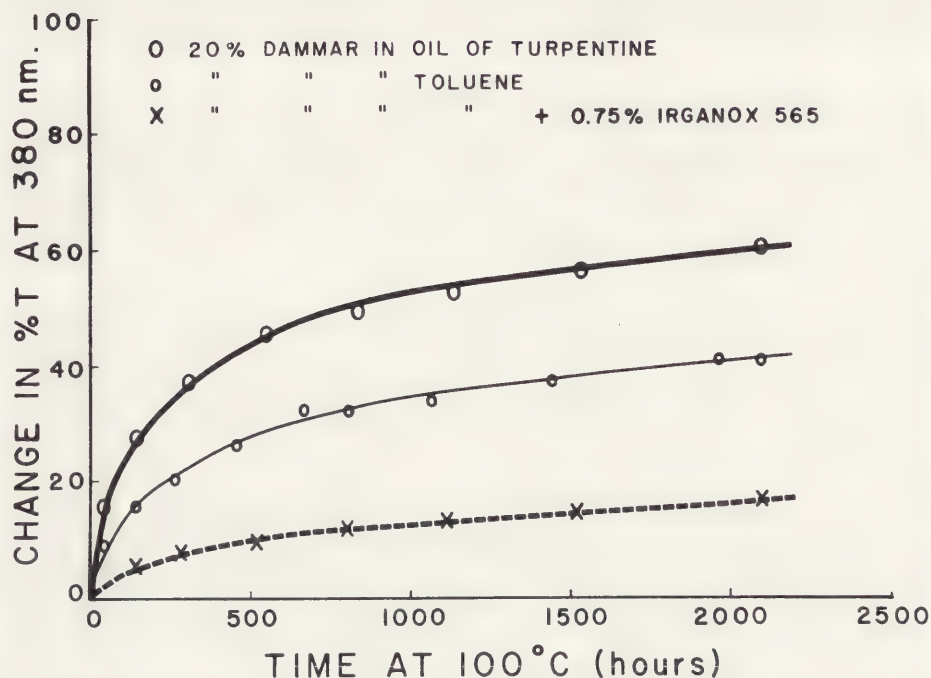


FIG.1 Yellowing curves for dammar varnish films artificially aged at 100°C.

In order to correlate accelerated aging at 100°C and normal room-temperature ageing, a direct comparison of the two was made. It is true that yellowing at room temperature is a relatively slow process but owing to the extreme sensitivity of the spectrophotometer, very small changes in the transmittance can be measured. Figure 2 illustrates the change in %T at 380 nm against the number of days at room temperature for three sets of films. Each set contained five samples. The films prepared with the oil of turpentine as solvent have, after almost two years, reached a value of 11.9, just slightly above the 'just perceptible level'. Those prepared with toluene had reached a value of only 3.5% after 615 days. A very small change, 0.5%, was measured for the stabilized films.

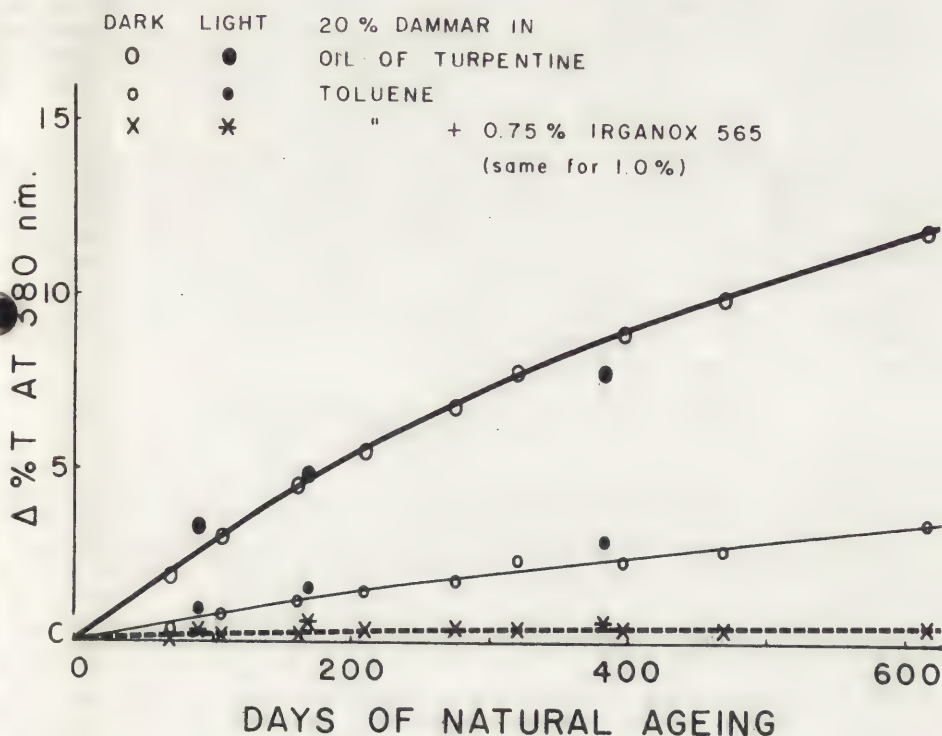


FIG.2 Yellowing curves for naturally aged dammar varnish films.

By comparing the two sets of ageing curves, a correlation can be established and the equivalent time to reach a change in $\%T$ of 20 at room temperature can be calculated. It was found that for films prepared with toluene, it would take 22 years to reach this limiting point whereas the films prepared with oil of turpentine would take only four years. The stabilized films would reach a value of 17 after approximately 350 years.

All fifteen films have been recently retested after a total natural dark ageing period of 4½ years. The average of the five dammar films originally prepared with oil of turpentine as solvent have now reached a yellowness index of 19.6 and

were all visibly yellow. The films prepared with toluene as solvent have now yellowed 5 units, still undetectable to the average observer. The stabilized dammar films have remained unchanged at 0.5 units. These recent measurements confirm once again the excellent effectiveness of Irganox 565 at reducing the yellowing rate of dammar varnish.

Although yellowing of dammar appears to be predominantly a thermal process rather than photochemical, the role of light in the yellowing cannot be discounted. Room temperature ageing with exposure to 700-1000 lux of light indicated that in some cases, the rate of yellowing was slightly higher for those samples exposed to light. However, the proportional decrease in yellowing rates due to the addition of antioxidant was unchanged. Results for dark and light ageing are compared in figure 2.

Solubility changes in Dammar Varnish

The decrease in solubility of dammar resin due to oxidation has been well documented [3,4]. Certain inhibitors such as antioxidants and ultraviolet absorbers can retard the rate of oxidation of surface coatings. The effectiveness of any given inhibitor can only be determined with certainty by carrying out accelerated ageing tests. Because Irganox 565 can reduce the yellowing of dammar this need not necessarily mean that it can similarly retard the decrease of solubility due to photo-oxidation. There is indeed no reason why it could not even accelerate insolubilization. To clarify this situation, photochemical ageing in a Weather-ometer at room temperature was undertaken. [5]

A plot of removability versus time of exposure is shown in Figure 3. As expected, the unstabilized dammar film becomes increasingly insoluble and requires stronger solvent to remove it after ageing. The solubility of the stabilized film does not decrease as rapidly. The improvement may not be overwhelming yet, in the light of reduced yellowing rates, it is sufficient to render dammar varnish a suitable picture varnish.

It may be of interest to point out that there exist essentially two patterns of oxidation in dammar varnish films: photo-oxidation which leads primarily to increased insolubility, and thermal oxidation, the principal effect of which is yellowing. Even after 768 hours in the Weather-ometer (22°) there was no visible yellowing of the films (though in view of the high light levels involved, bleaching of initially formed yellow compounds could be considered an alternative reason for this). Furthermore the solubility of dammar films aged in a dark oven at 100°C [2] was not found to be significantly changed even after 2100 hours.

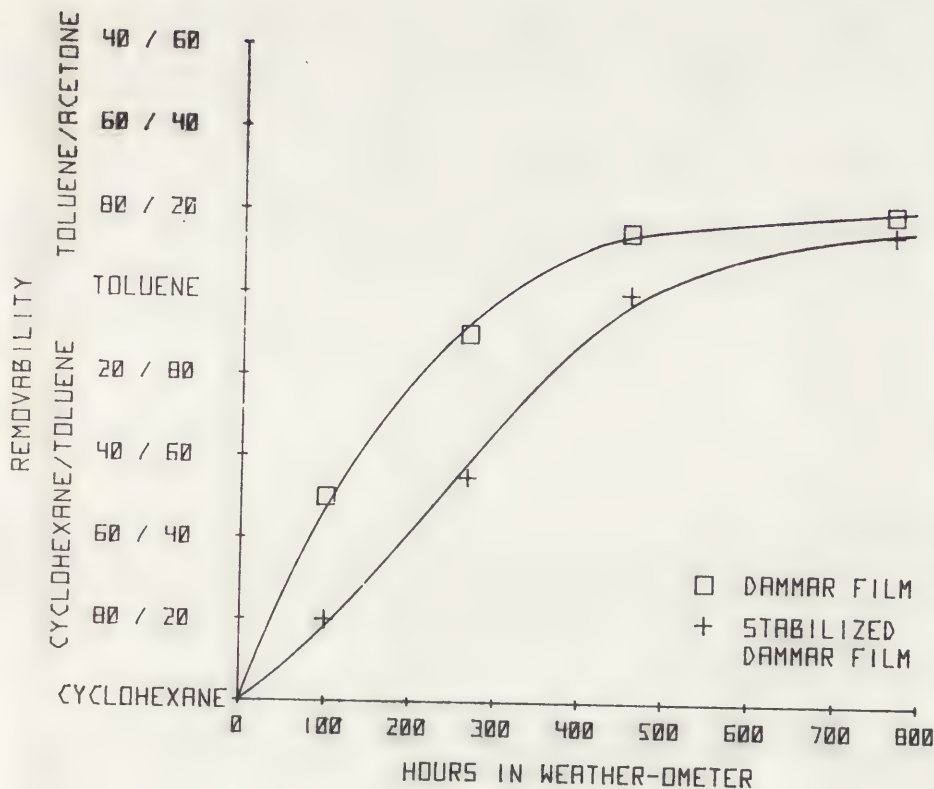


FIG.3 Removability of stabilized dammar films as a function of accelerated ageing time. An upward curve indicates a decrease in solubility.

In light of these results, the general approach to accelerated ageing techniques should be revised somewhat. Although photochemical ageing may occur at a faster rate than thermal reactions, in most museum conditions light levels are considerably lower than normal situations, thus shifting the emphasis to thermal rather than photochemical reactions. This will be discussed further in a subsequent section of this paper.

Use of stabilizers in Ketone Resin N varnish

Whereas discolouration processes may be caused by both thermal and photochemical mechanisms, the changes in solubility of coatings as a function of time appears to be predominantly photochemical in nature. As mentioned in the

previous section, highly yellowed dammar films aged in a dark oven at 100°C remained soluble in a weak solvent such as cyclohexane, yet their appearance were similar to that of a very old varnish. Any studies done on insolubilization should concentrate on photochemical procedures such as exposure in a Fade-ometer, Weather-ometer or other high intensity light chamber.

Ketone Resin N, an increasingly popular synthetic resin, suffers from decreased solubility as it ages. Caused by photochemical oxidation and cross-linking, the rate of change in solubility can be decreased significantly by the addition of antioxidants and UV absorbers, as shown by the work carried out in our laboratories. [6]

A total of 10 antioxidants and UV absorbers were evaluated at various concentrations. Typical results are shown in figures 4 to 7.

A notable decrease in the rate of cross-linking of Ketone Resin N was evident. Pure Ketone Resin N would require a solvent slightly stronger than toluene to remove it after 200-300 hours of accelerated ageing. With 10% Uvinul D-49 added, the solubility remained much higher. After 200 hours, it was still easily removed by 80/20 cyclohexane / toluene. After 900 hours, it was still soluble in 5/95 cyclohexane/toluene.

Cyasorb UV 24 also afforded similar protection as well as four of the five antioxidants. Uvinul 400, Tinuvin 327 and Tinuvin P were not as effective. Irganox 565 had little or no effect on the ageing of the varnish.

A combination of antioxidant and UV absorber proved to be the best (see figure 7).

Eventual occurrence of cross-linking after prolonged ageing seems unavoidable even in the stabilized film. We can only suggest hypothetical explanations. In the case of UV absorbers, the uppermost layer of varnish is not as well protected as the underlying layer of varnish. Imagine that the actual polymer film is divided into small layers. As the UV radiation goes through each subsequent layer, more and more is filtered out by the absorber. Even though the final amount of UV that is filtered is high (90), much of the UV was still transmitted through the first very thin layers. These layers are therefore subject to some cross-linking which might account for the eventual decrease in solubility indicated on the graphs.

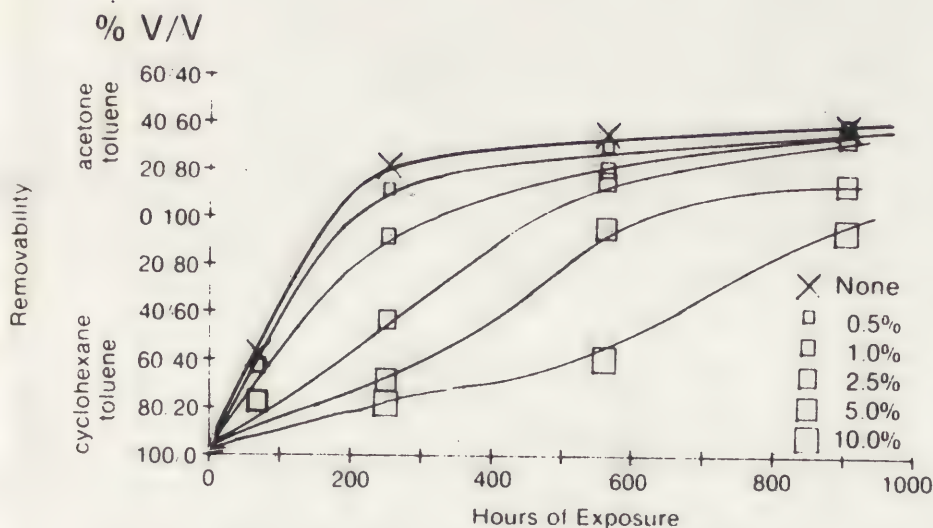


FIG.4 Changes in removability of Ketone Resin N varnish films containing Uvinul D-49. Similar curves were obtained for Cyasorb UV24.

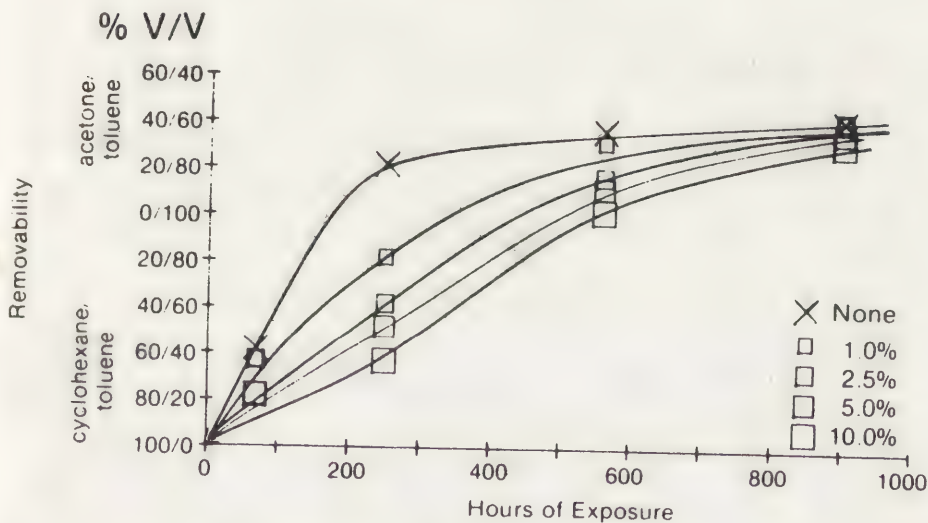


FIG.5 Changes in removability of Ketone Resin N varnish films containing Uvinul 400.

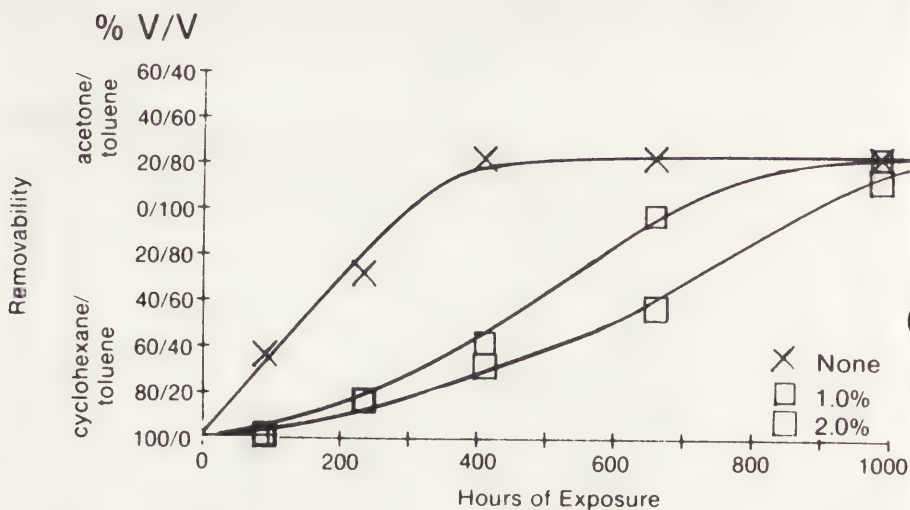


FIG. 6 Typical curves obtained for the changes in removability of Ketone resin N containing Irganox 1093, 1035, 1010 or 1076.

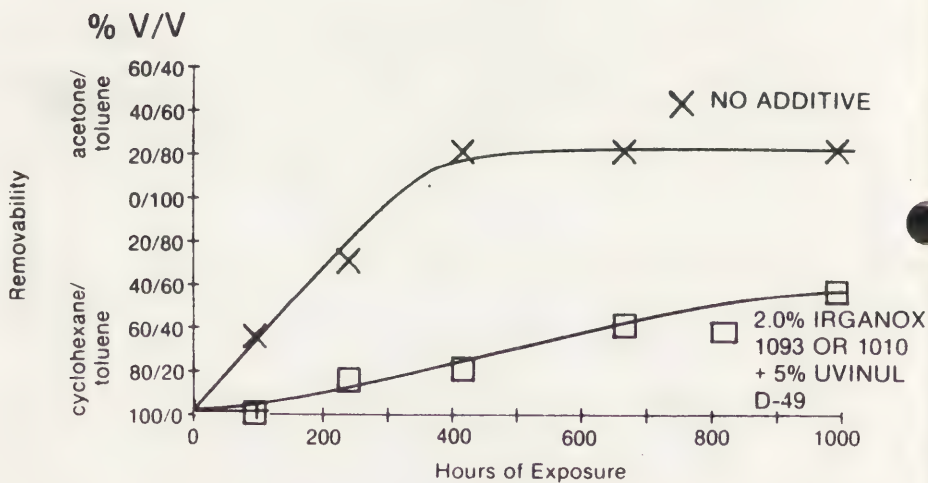


FIG. 7 Maximum protection as afforded by the combination of antioxidant and Uvinul D-49 as shown in this graph.

Standard accelerated ageing techniques

Earlier, we eluded somewhat to the problem of utilizing proper accelerated ageing techniques. Standardization is certainly the ultimate goal of this committee. Yet, it is not always clear what technique is most suited for studying specific physical or chemical parameters. For example, the yellowing of varnishes, particularly dammar, is often thought to be caused by photochemically induced reactions. Past work by this and other authors have shown that aged dammar films are bleached by daylight and sunlight. In light of this, how can one still consider solely photochemical studies when investigating discolouration problems?

In many instances, materials used in art conservation will be exposed to low levels of illumination whose ultraviolet radiation component will have been reduced to minimal proportions. This will have come about either by proper choice of lamps and/or by the utilization of UV absorbing filters. Backing board for canvas paintings for example could not be evaluated on photochemical stability alone. So called "dark reactions" would undoubtedly play the major role in their deterioration. In this case thermal accelerated ageing should be used to study its durability. Thus the end-use of a product will invariably determine the type of accelerated ageing.

Recently, studies carried out in the author's laboratory on the yellowing of epoxy adhesives [7] clearly illustrated the need for a sound rational approach to accelerated ageing methods.

It was evident from the onset of the project that both thermal and photochemical techniques would be involved. Our concern revolved around the yellowing of epoxy adhesives used in the repair of clear, colourless glass artifacts. Their normal environment would include controlled light levels, perhaps never exceeding 300 lux. UV radiation would also be low. Thermal ageing is therefore absolutely required. Since epoxies are also used in applications when light levels might be excessive, photostability can become important and a separate study of the latter was also deemed necessary.

Thermal ageing was done in dark convection ovens at five temperatures: 50°C, 63°C, 75°C, 87°C and 100°C. To minimize errors, we included five samples for each temperature.

Thickness profiles for all films, as measured on an accurate displacement probe, were used to correct all absorbance values.

The application of the Arrhenius equation with extrapolation to room temperature provided us with an accurate correlation to room temperature conditions. Fig. 8 illustrates the yellowing rates for a typical epoxy formulation. Since yellowing rates appeared to be a linear relationship, the slope of the line provided us with precise rate constants (K_t) for each temperature. The effect of temperature on the rate of chemical reaction is described by the Arrhenius equation

$$\log K_t = \frac{E_a}{2.303R} \frac{1}{t} + \log A$$

where

t = temperature in °Kelvin
 R = gas constant
 E_a = activation energy
 A = integration constant

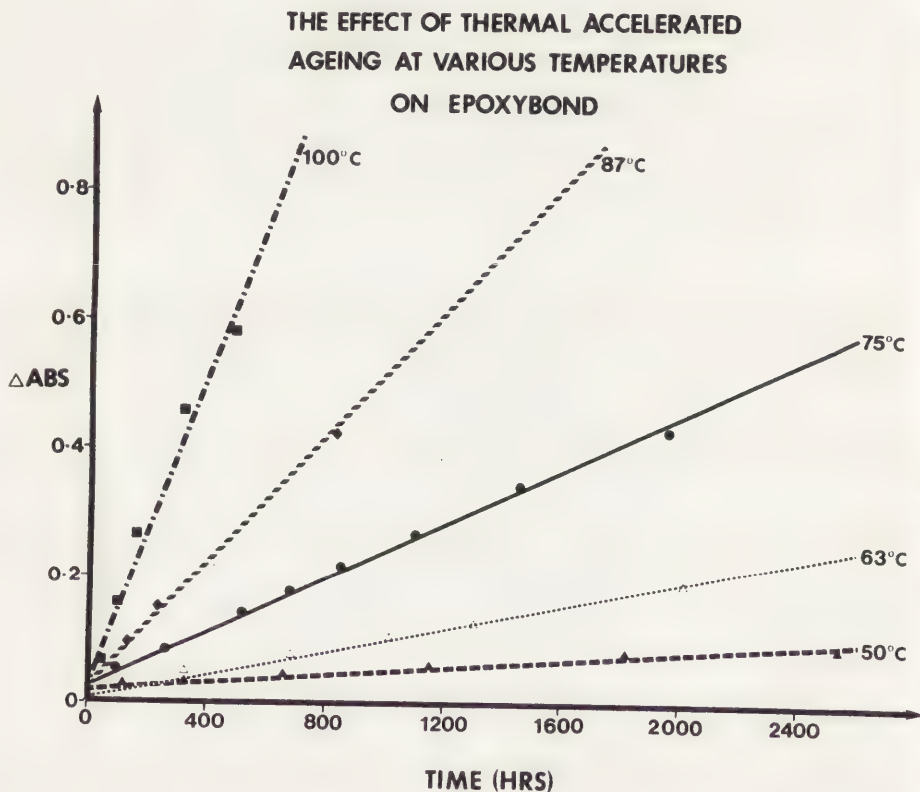


FIG.8 Yellowing curves obtained for a typical epoxy adhesive. The rate constants K_t can be obtained from the slope.

When $\log k_t$ is plotted against $1/t$ a straight line results as shown in figure 9. A direct extrapolation to room temperature provides us with $K_{22^\circ\text{C}}$, the rate constant at room temperature. Straight line fits were exceptionally good, indicating the applicability of this approach.

ARRHENIUS PLOT FOR EPOXYBOND

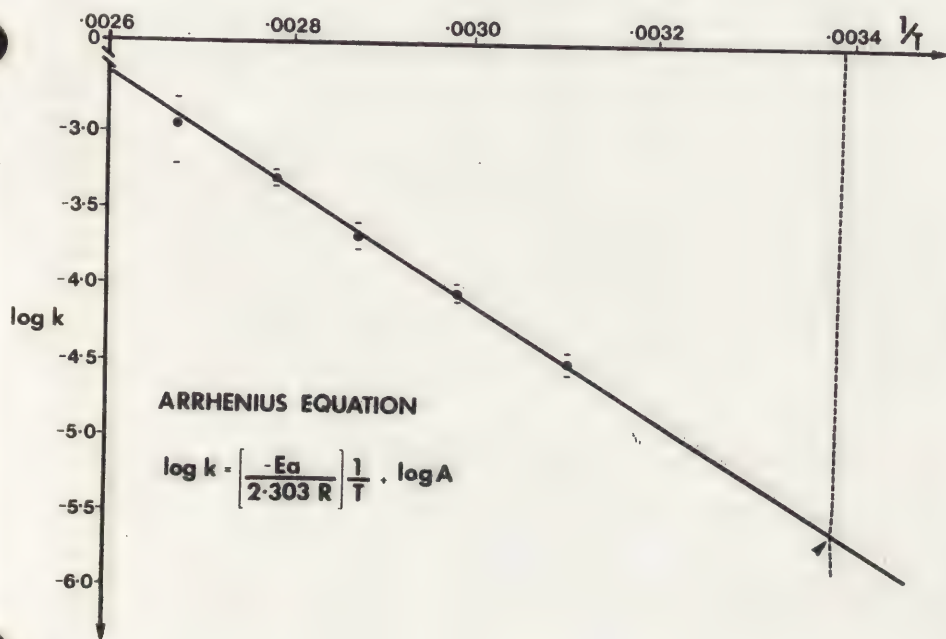


FIG.9 A plot of $\log K_t$ vs $1/t$ from which $K_{22^\circ\text{C}}$ can be calculated.

Photochemical ageing was done in a Weather-ometer. Here, traditional techniques were used except for one important factor: chamber temperature was maintained at 22°C ($\pm 2^\circ\text{C}$) throughout the ageing period. This was achieved by the use of infrared absorbing filters on the lamp and cooling coils in the conditioning chamber. By doing this, we have attempted to eliminate (or at least reduce to insignificant levels) the contribution to yellowing from thermochemical reactions. Treatment of the data included direct use of cumulative theories and a multiplication factor proportional to UV radiation content.

This approach allowed us to obtain two separate yellowing rates: one thermal and another strictly photochemical. By knowing the conditions in which the product will be subjected to, it is possible to predict which of the two will be rate determining. Results obtained for epoxy adhesives indicated that at lower light levels (300 lux) thermal reactions are more important. On the other hand, outside exposure to intense illumination would shift the emphasis to photochemical reactions and these would overtake thermal yellowing. Combined effects could only be hypothesized since synergistic effects can occur.

This approach will be tested further when we begin our studies of polyvinyl acetate adhesives. A similar differentiation of ageing mechanisms will be attempted and we feel confident that this approach will again provide meaningful results. We would hope that standardization of accelerated ageing techniques will be developed from this and other work in the conservation research field.

References.

1. Feller R.L., and Curran M., "Solubility and Crosslinking Characteristics of Ethylene/Vinylacetate Copolymers" Bulletin of the American Group-I.I.C., Vol. 11, No.1, 1970.
2. Lafontaine, R.H., "Decreasing the Yellowing Rate of Dammar Varnish Using Antioxidants" Studies in Conservation, 24(1979), 14-22
3. Feller, R.L., and Baillie, C.W., "Solubility of Aged Coatings Based on Dammar, Mastic and Resin AW-2", Bulletin of the American Group-IIC, 12(2)(1972), 72-81
4. Feller, R.L., and Curran, M., "Changes in Solubility and Removability of Varnish Resins with Age", Bulletin of the AIC, 15(2)(1975), 17-26
5. Lafontaine, R.H., "Effect of Irganox 565 on the Removability of Dammar Films" Studies in Conservation, 24(1979), 179-181.
6. Lafontaine, R.H., "The Effect of Inhibitors on the Removability of Aged Ketone Resin N Varnish Films," Journal of the IIC-C.G., 3(2), 7-12.
7. Down, J.L. and Lafontaine R.H. "The Yellowing of Epoxy Adhesives", manuscript submitted for publication.

81/16/5-16

Materials and Instrumentation

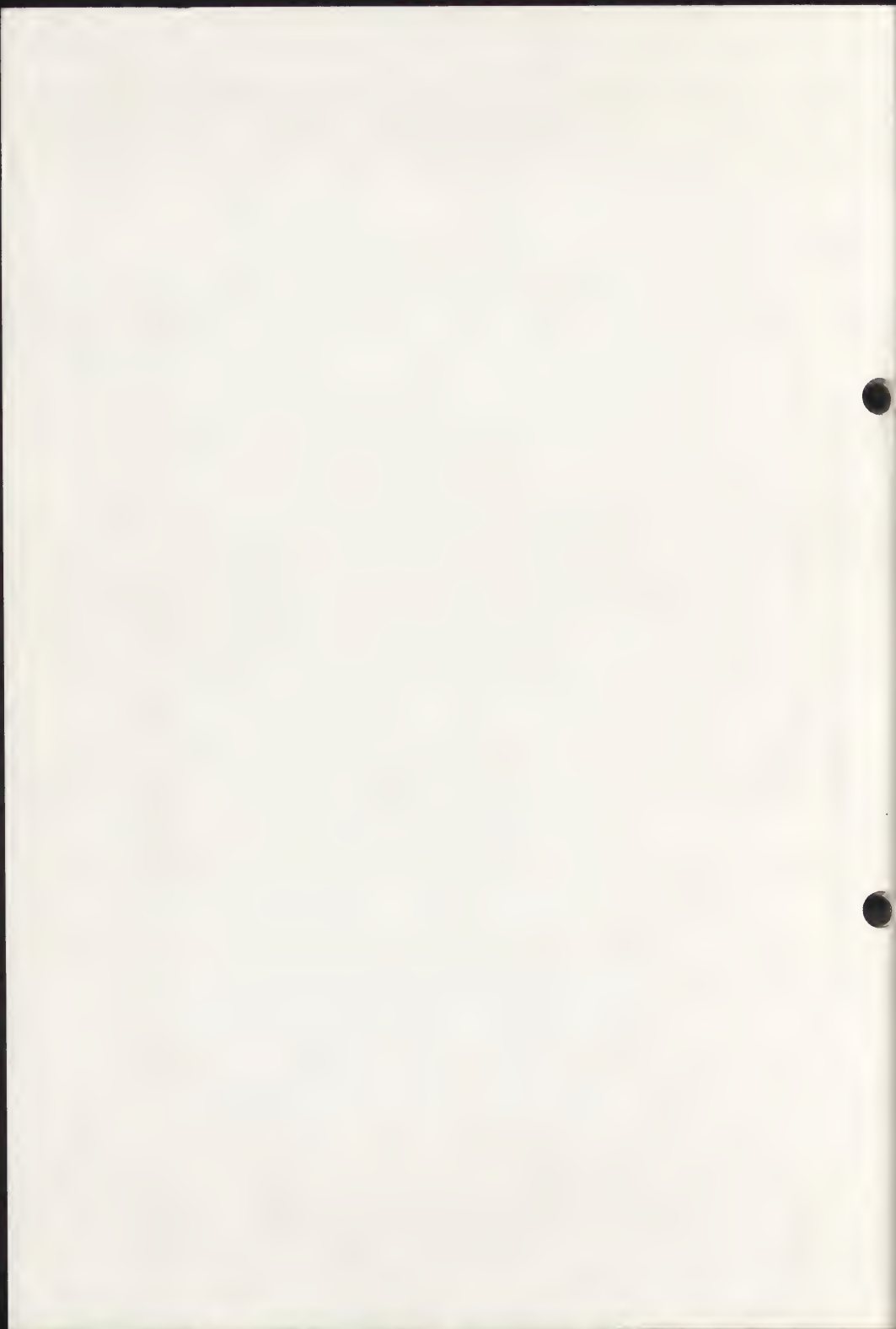
- Ketone Resin N: BASF (Canada) Ltd, 5850 Cote de Liesse,
Town of Mount Royal, Quebec, H4L 4V8 Canada
- Uvinul's: GAF Corporation, available from Chemical
Developments of Canada Ltd., 104 Doryon
Ave., Pointe Claire, Quebec, H9R 3T5 Canada
- Cyasorb UV 24: American Cyanamid Co., available from
Cyanamid of Canada Ltd., 2031 Kennedy Road,
Scarborough, Ontario, M1P 2M4, Canada
- Tinuvin's and Irganox's: Ciba-Geigy Canada Ltd., 858 York
Mills Road, Don Mills, Ontario, M3B 3A8
Canada
- Weather-ometer & Fade-ometer: Atlas Electric Devices Co.,
4114 N. Ravenswood Ave. Chicago, IL 60613.
Available in Canada from J. B. Atlas Co.,
44 Fasken Drive, Unit A, Rexdale, Ontario,
M9W 1K5, Canada.

Table I - Effect of antioxidants on the yellowing rate of dammar

[illegible]

Antioxidants producing highly coloured solutions

N-Lauroyl-p-aminophenol
N,N'-bis-1,4-dimethylpentyl-p-phenylenediamine
di-p-methoxydiphenylamine
-dodecyl-1,2-dihydro-2,2,4-trimethylquinoline
N-Isopropyl-N-phenyl-p-phenylenediamine
N,N'-dephenyl-p-phenylenediamine
B-naphthyl-p-phenylenediamine
N-phenyl-N'-cyclohexyl-p-phenylenediamine
N-phenyl-2-naphtylamine
N-phenyl-1-naphtylamine
m-Touluylenediamine



81/16/6

PRESERVATION OF AGED PAPER BY ALKOXYSILANES

C.M.Paleos, E.E.Mavroyannakis and
Irene Cypriotaki

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Protective Coatings,
Traditional and Modern

Figure 1

PRESERVATION OF AGED PAPER BY ALKOXYSILANES

C.M.Paleos, E.E.Mavroyannakis and Irene Cypriotaki

Nuclear Research Center "Demōkritos"
Departments of Chemistry and Technological Applications
Aghia Paraskevi
Attikis,
Greece

Irene Cypriotaki
Athens Paper Mill, S.A.
Athens
Greece

Abstract.

A method for the preservation of aged paper by the use of alkoxyisilanes is introduced. Alkoxyisilanes are easily applied to the paper but their curing requires several hours. Busting and tensile strength of treated paper showed satisfactory improvement whereas its elongation decreased. Furthermore, treated paper exhibits high hydrophobicity and a remarkable light stability both properties contributing to its preservation.

Introduction.

A serious problem associated with ancient or aged bibliographic material is the reinforcement and in general, the preservation of paper documents that had been rendered fragile. This fragility and also discoloration are phenomena caused by oxidative and hydrolytic processes which affect cellulose of the paper (1,2). In addition, the mechanical strength of the paper is also reduced, by wear and micro-organism attack. Deacidification, fumigation or sterilization are conservation processes that have to be applied. For deacidification successful methods have been reported including aqueous (3,4) non-aqueous (5) and mass-deacidification (6,7) procedures. Fumigation processes have also been developed (8) by the use of polymers which further protect them from environmental influences. Polymers that have been employed for this purpose include polyvinylacetate (9), the sodium salt of carboxymethylcellulose (2), polyvinylcohol (10) or polyacrylamide (11).

In this first report the use of alkoxyisilanes in the treatment of aged paper is introduced. Silica and alkylpolysiloxanes which are formed by hydrolysis of alkoxyisilanes and alkylalkoxyisilanes and subsequent polymerization of their hydrolysis products may preserve aged paper.

Chemistry and Application of Alkoxysilanes to Paper

It is well-known that alkoxysilanes and alkylalkoxysilanes have widely been employed for the preservation of ancient stone monuments (12-14). In this work the suitability of these compounds will be tested for the preservation of aged paper. Triethoxysilane, for example in the presence of humidity with a specific catalyst hydrolyzes to silicic acid which is unstable and converted to silicon dioxide, a natural binder with the liberation of water. On a similar fashion triethoxymethylsilane or trimethoxymethylsilane are initially hydrolyzed while their reaction product reverts to methylpolysiloxanes. The methyl group of this polysiloxane is responsible for the water repellency.

In applying this method, aged book pages were treated with an alkoxysilane formulation sold under the commercial name "Strengthening agent H" manufactured by Wacker Chemie. This formulation between other compounds contains an alkoxysilane, alkylalkoxysilane and alkylpolysiloxane as water-repellent agents, and also a catalyst. Our results on the treatment of aged paper were compared with the ones obtained by treating Whatman No 4 filter paper under similar conditions. The wettability of both types of paper was excellent and the samples after being immersed for a few seconds in the commercial material they were allowed to stay in humid environment, at room temperature, for curing.

Results and Discussion

The weight loss of aged book pages and of Whatman No 4 filter paper as a function of the curing time or otherwise the curing curves of the material retained by the papers is shown in Fig. 1.

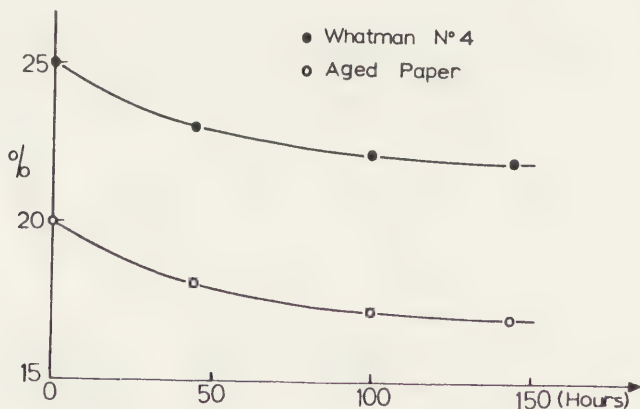


Fig. 1. Curing curves of Strengthening Agent H retained by aged book pages and Whatman No 4.

It is seen from these curves that curing is completed in about 150 hours, for both samples. The weight increase remaining after curing is 22% for Whatman No 4 paper and 17% for the aged book pages. Apparently the higher porosity of Whatman paper contributed to its better impregnation. A thickness increase of the order of 0.01 mm was measured for Whatman paper whereas such thickness increase could not be detected for aged paper.

The treated samples were subsequently tested for an improvement of their mechanical properties. Thus, in Table I below some of the mechanical properties of treated samples are compared with those of the untreated ones.

Method of Testing	Untreated ³		Treated ³	
	Whatman No4 Aged Paper		Whatman No4 Aged Paper	
Bursting ₁ Strength (Kg/m ² /m ²)	8.3X10 ³	8X10 ³	1.86X10 ⁴	1.0X10 ⁴
Bursting Strength ratio(Kg/gr)	89	158	165	171
Tensile ₂ Strength (Kg/15mm)	2.5	2.9(MD) 1.9(CD)	5.1	3.4(MD) 2.4(CD)
Elongation ² %	2.3	2.0(MD) 2.0(CD)	2.0	2.0(MD) 1.8(CD)

1. According to TAPPI T 403 05 - 76 standards

2. " " " T 404 ts - 66

3. Batches of 10 samples

Table I. Some of the mechanical properties of untreated and treated Whatman No 4 paper and aged book pages.

From these results it is evident that treated papers show a bursting strength improvement and primarily Whatman No 4. Furthermore aged paper presents a higher burst strength ratio than Whatman No 4 but the latter exhibits a more pronounced improvement. Bursting strength results are partly due to the higher retention of material by Whatman as compared to the lower one of aged paper. Tensile strength values of aged paper shown in Table I refer to 15 mm wide strips cut in machine (MD) and in the cross direction (CD). For Whatman No 4 the average values for these two directions are included. Concerning tensile breaking strength a very good improvement has been obtained for Whatman No 4 paper while that of aged paper has been only satisfactorily improved. The results are, as expected, in line with those of bursting strength. Paper elongation shows a decrease in both kinds of paper. The smaller decrease of

aged paper in comparison to Whatman No 4 is very probably due to the lower material retention.

The extent of these properties improvement cannot originate only from differences in material retention. It has therefore to be assumed that alkoxysilanes are not as effective towards aged paper as they are with Whatman No 4. This also may be due to the previous treatment that printed paper had been subjected to.

The treating agent shows an excellent compatibility with these papers and they both exhibit - after treatment and curing - high hydrophobicity which contributes to their preservation.

Treated Whatman No 4 and aged paper also show excellent stability to light. Thus, no perceptible discoloration was observed by exposing treated samples in an SUNTEX accelerated aging apparatus for 46 days i.e. for a period corresponding 2 years of sunlight exposure.

The disadvantage of this method seems to be its irreversibility. It does not look however probable that one should ever reach to the point to remove this "protecting" material.

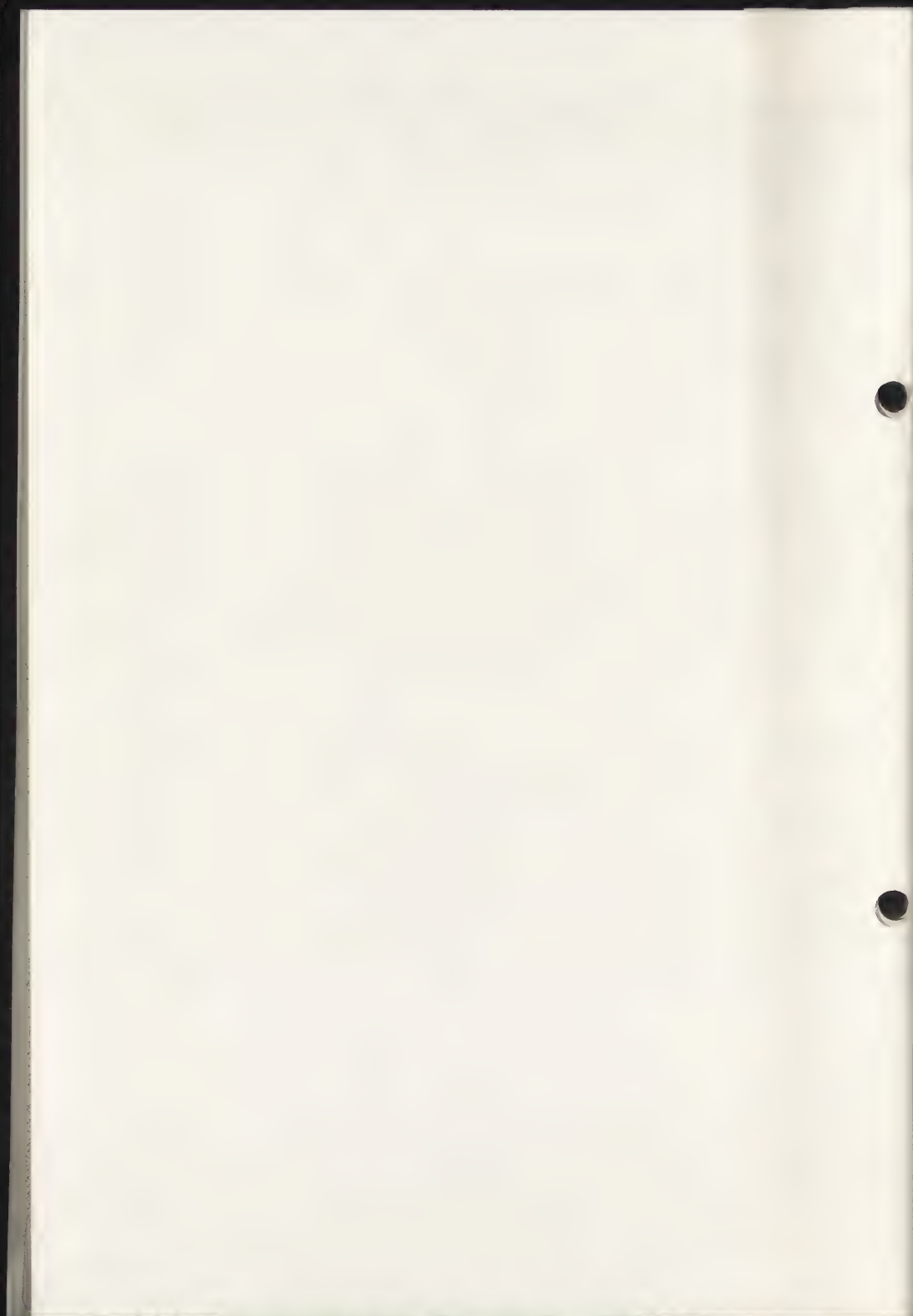
The material remaining after curing by its nature is stable and harmless and particularly if one considers the environmental conditions that are usually prevailing in museums and libraries. The disadvantage therefore of irreversibility is not a serious one in this case.

In conclusion, the method is worth considering since it provides a satisfactory preservation to the aged paper.

References.

1. A. Zappala and P.L. Pendola (78/14/18), Paper presented at "ICOM Committee for Conservation" 5th Triennial Zagreb, October, 1978.
2. R.A. Stuhrke, in "Preservation of Paper and Textiles of Historic and Artistic Value", J.C. Waiiams Ed., Advances in Chem. Series, Vol. 164, 1977 p. 24.
3. Schierholtz, U.S. Patent 2.033,452 (March 10, 1936).
4. W.J. Barrow "Permanence/Durability of the Book III" "Spray Deadification" Dietz Press, Richmond, 1964.
5. G.B. Kelly, Jr., L.C. Tang and M. Krasnow in "Preservation of Paper and Textiles of Historic and Artistic Value" J.C. Waiiams Ed. Adv. in Chem. Series, Vol. 164, 1977, p. 62.
6. B.F. Walker in "Preservation of Paper and Textiles of Historic and Artistic Value", J.C. Waiiams, Ed., Adv. in Chem. Series, Vol. 164, 1977 p. 72.
7. R.D. Smith in "Preservation of Paper and Textiles of Historic and Artistic Value", J.C. Waiiams, Ed. Adv. in Chem. Series, Vol. 164, 1977 p. 149.
8. D. Fischer, in "Presentation of Paper and Textiles of Historic and Artistic Value", J.C. Waiiams, Ed., Advances in Chem. Series, Vol. 164, 1977 p. 139.

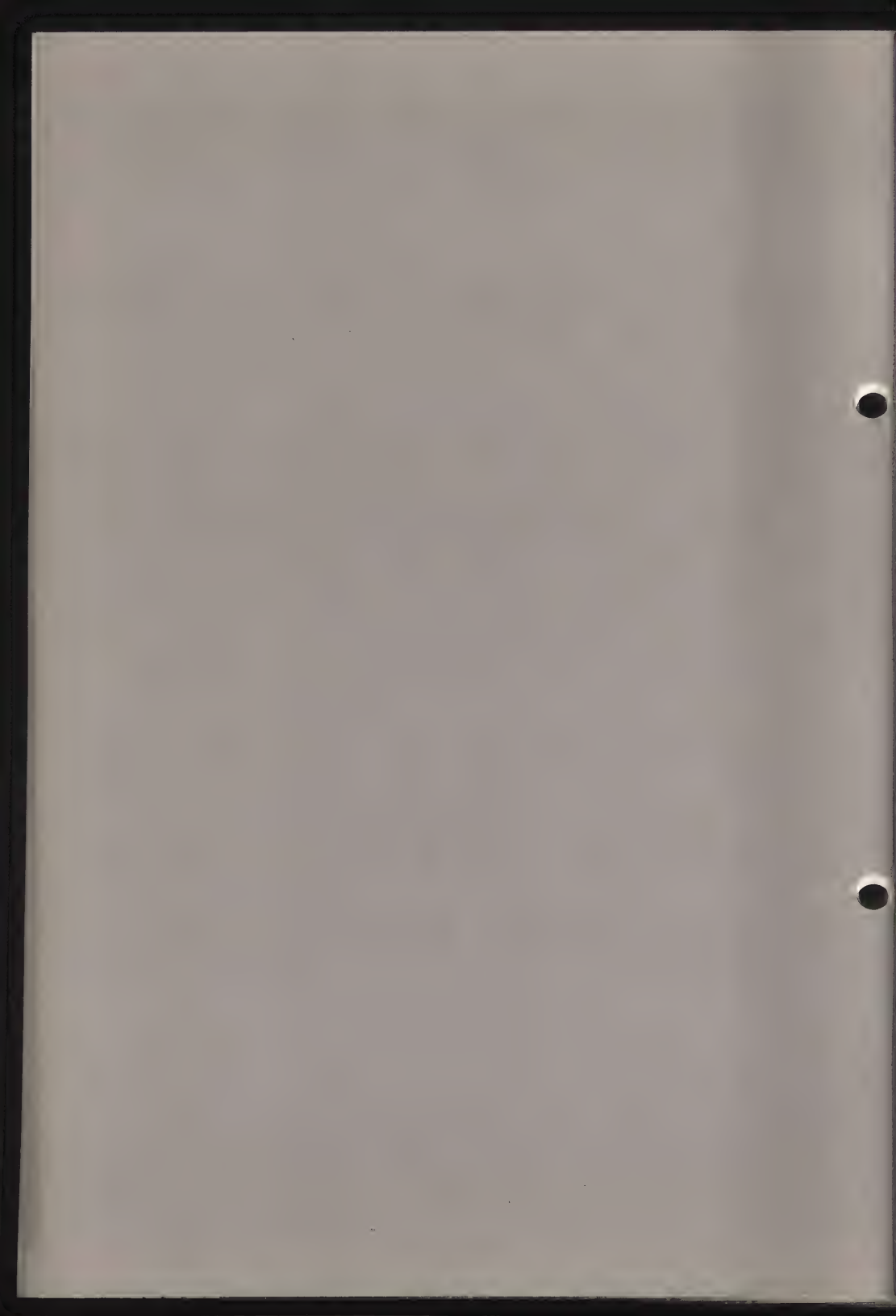
9. J. Riederer, Naturwissenschaften, 65, 217 (1978).
10. M.G. Blank (78/14/6), Paper presented at "ICOM Committee for Conservation" 5th Triennial Meeting, Zagreb, October (1978).
11. J.P. Nynksha (78/14/13), Paper presented at "ICOM Committee for Conservation" 5th Triennial Meeting, Zagreb, October, 1978.
12. C.A. Price, Chem. Brit, 11, 350 (1975) and references cited therein.
13. L. Arnold, D.B. Honeyborne and G.A. Price, Chem. and Ind., 345 (1976).
14. C.M. Paleos and E.G. Mavroyannakis (78/21/1) Paper presented at "ICOM Committee for Conservation" 5th Triennial Meeting, Zagreb, October, 1978.



NUCLEAR APPLICATIONS TO CONSERVATION

Coordinator : Chr. de Tassigny (France)

Assistant coordinator: R. Ramière (France)



GROUPE DE TRAVAIL APPLICATIONS DES TECHNIQUES NUCLEAIRES
A LA CONSERVATION SEPTEMBRE 1978

Assistant coordinator: R. Ramière

CENG Grenoble Sarr
B.P. no. 85 Centre de Tri
38041 Grenoble Cedex
France

La première réunion du groupe de travail "Applications des Techniques Nucléaires à la Conservation" a eu lieu au 3ème Congrès du Comité pour la Conservation à Madrid. Il avait pour objet d'assurer notamment une liaison entre les laboratoires utilisateurs de techniques nucléaires et coordonner leurs travaux dans l'étude de biens culturels et la mise au point de procédés de conservation.

Depuis la 4ème réunion du Comité de Conservation à Venise en 1975, les travaux du groupe ont reçu une orientation plus spécifique: la mise au point et l'application de nouvelles méthodes de conservation.

Les activités ont couvert les applications des propriétés du rayonnement gamma à deux domaines de la conservation des matériaux:

- la désinfection de matériaux contaminés par des insectes ou des attaques microbiennes.
- la consolidation de matériaux poreux très altérés: bois, bois gorgés d'eau, pierre, terre cuite, os etc...

L'état d'avancement des travaux diffère dans chacun des domaines.

Au stade de l'étude ou de la phase expérimentale on peut citer:

- La consolidation des bois revêtus (bois polychromés)
- la consolidation des matériaux pierreux (calcaires, grès...) et terres cuites, argiles, os.

Au stade de l'application ou de l'exploitation de routine:

- la désinfection du bois ou de matériaux composites
- la consolidation de bois non revêtus (ébénisterie)
- la consolidation de bois gorgés d'eau.

A ce stade des travaux du groupe, beaucoup d'études restent encore à effectuer pour améliorer les techniques ou pour les

étendre à d'autres types de matériaux. Cependant, l'existence de ce groupe depuis 1971 a permis de montrer que les techniques nucléaires représentent un apport intéressant à la panoplie des méthodes de conservation.

Il apparaît donc maintenant plus conforme à l'esprit du fonctionnement des groupes de travail de provoquer "l'éclatement" du groupe "Applications nucléaires". C'est dans ce sens qu'il a été proposé au Conseil de direction du Comité de Conservation de dissoudre ce groupe et que dorénavant les études traitant des techniques nucléaires soient présentées dans les groupes de travail traitant spécifiquement des matériaux concernés (bois, pierre etc...)

R. Ramière

Le Conseil de direction a suspendu Le Groupe de travail "Applications nucléaires à la conservation" hors d'une réunion à Cardiff le 20 mars 1981.

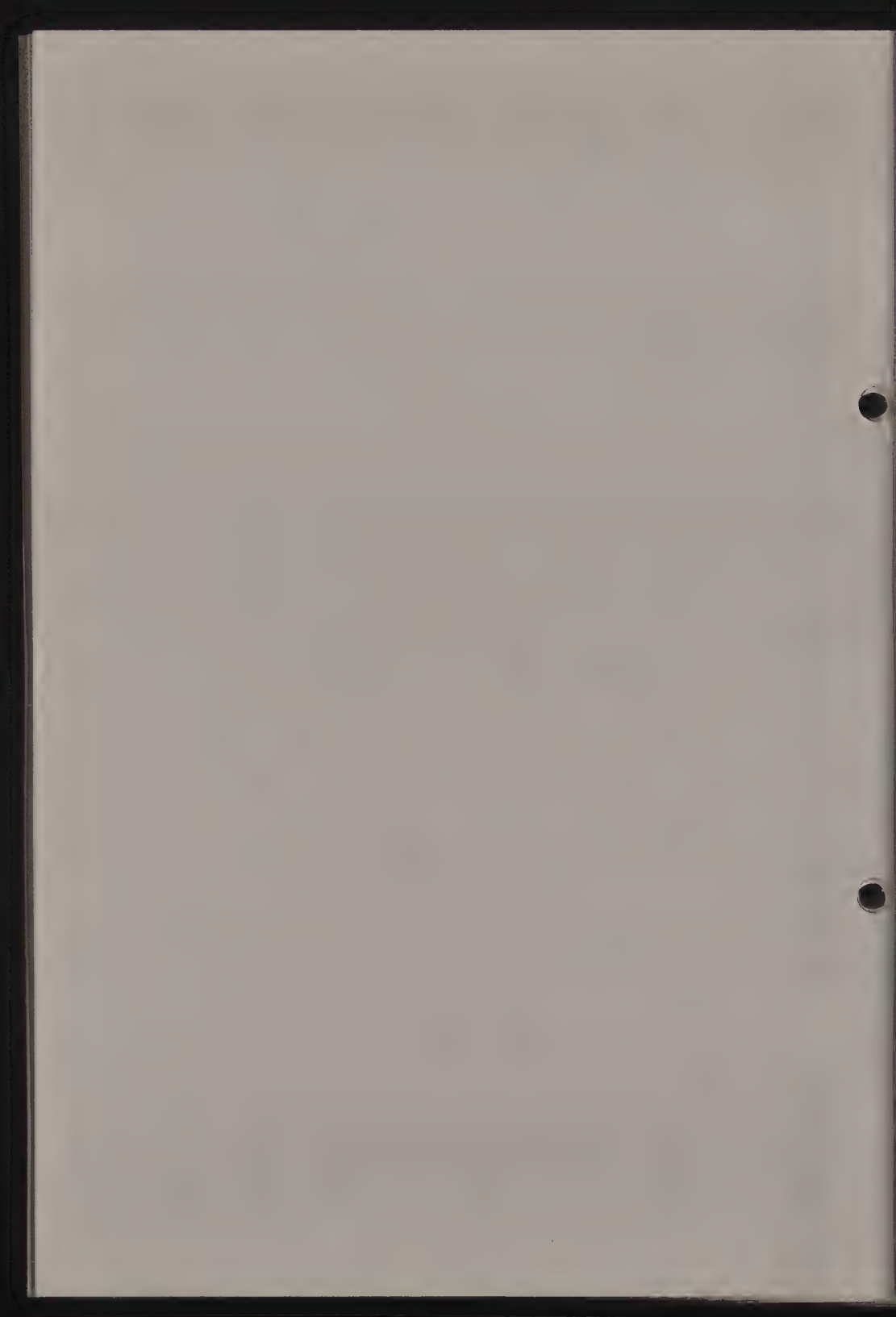
81/17/1

AGEING OF REINFORCED ANCIENT MATERIALS BY
GAMMA RAY METHODS

E.G.Mavroyannakis

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Nuclear Applications to
Conservation



AGEING OF REINFORCED ANCIENT MATERIALS BY GAMMA RAY
METHODS

E.G.Mavroyannakis

Nuclear Research Center "Demokritos"
Athens
Greece

Abstract

The acceptability of various methods applied for conservation purposes of ancient materials, depend mainly on their satisfactory results for long periods of time after treatement. This important point is discussed in this paper, taking into consideration materials treated some years ago by gamma ray methods, and aged under various conditions.

The discussion is concerned with ancient wood, fireclays, stones, bones and marbles. Ageing tests are performed under free atmospheric conditions, ambient and accelerated conditions .

Introduction

The reinforcement of ancient materials by the use of gamma ray methods, has already been established /1//2//3//4-6/. However, some points require clarification because of their importance in the field of conservation of cultural property. Between these is ageing of treated materials under more or less well defined environmental conditions. Consolidation in general imposes two different classes of problems :

- I- the problems of treatment, which can be considered solved,
- and 2- the problems of the after treatment durability, which must still be studied .

The problems of durability are related to the physical, chemical and biological behavior of the material after consolidation. The life of the objects after treatment must be as long as possible with minimum depreciation of their value /5/. This means that their ageing must be slower than for untreated objects. Although it is not our purpose to describe the mechanisms of materials degradation, it is useful to have a comprehensive picture of them. The fundamental processes of degradation can be represented schematically as in Fig. I. This representation shows the mutual relation between physical, chemical and biological processes of ageing as well as their interrelation. Any process can produce changes to the other two classes of processes. Biological processes for instance can produce physical and chemical processes and so on.

In the following paragraphs results of ageing for radiation consolidated materials under natural and accelerated conditions are reported.

General Considerations

Ancient materials studied in this report are treated by gamma ray methods, using synthetic resins as described elsewhere /1//2/. These materials as well as the monomers and ageing conditions are referred in Table I.

All consolidated materials show remarkable improvement of their properties, are more compact and less water absorbing than before treatment. It is

Ageing Processes

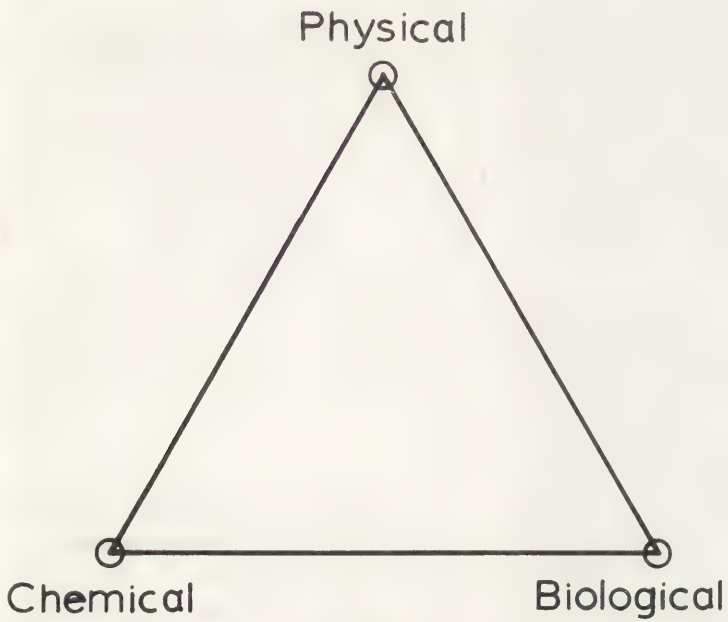


Fig. 1

however difficult to perform quantitative measurements in these materials, so our results are mainly qualitative.

Table I

Matrix Material	Monomer	Ageing Conditions
Wood	MMA, VA, S	Natural
Marble	MMA, S	Natural
Stones	MMA, S	Natural
Fireclays	MMA, VA, S	Natural and Accelerated
Bones	MMA, VA	Natural and Accelerated

S = Styrene-Polyester

VA = Vynil acetate

MMA = Methyl Methacrylate

Dry and Waterlogged Wood

Wood consolidation with synthetic monomers gives very satisfactore results even in cases of advanced deterioration, as happens for wood of ancient shipwrecks found under sea water. We have treated wood objects as shown in Table II, and the results are es-
thetically very good in all cases .

Ageing of the consolidated material for four years under ambient conditions does not show any sign of alteration . Tests performed under free atmospheric conditions of modern wood treated by gamma rays, show small cracks on their surface due probably to internal stresses. Under ambient conditions cracks have not been observed up to now for the same material. For ancient wood no cracks have also been observed, after four years of ambient ageing .

The appearance of treated material is remarkably natural and no sign of treatement is observed, although weight is increased more than 50o/o of dry material. Appreciable deformations have not been found and dimensional changes seems to be of the same order od magnitude of that produced by water absorption .

Up to now no biological degradation is observed, however, in order to test the durability of consolidated wood under accelerated conditions of biological attack, we have burried a number of radiation treated

and untreated modern wood samples for two years under the same conditions. After this period of time untreated wood was completely destroyed, while treated wood was nearly intact .

Table II (see Fig.I)

Wood Object	Age	Origin
Shipwreck	100 BC	Antikethyra
Wood stick	Roman	Megalopolis
Plow piece	- BC	-
Shipwrecks	19th Cent.	Navarinon

From the above results we can conclude that gamma rays consolidation of ancient wood, shows important properties for conservation purposes and no problems arise, in comparison to other methods of treatment /8//9/.

Reinforcement of Fireclays

Results of treatment of modern and ancient fireclays have already been reported in our previous reports, and problems arising during irradiation are mentioned /I/. Concerning however ageing we have exposed terracotta potsherds under various conditions as shown in Table III.

Table III

Ageing Conditions	Period of Time
Free atmospheric	5 years
Ambient	6 years
UV radiation (300W Lamp)	250 hours

Under free atmospheric conditions terracottas show more natural appearance, and under microscopic observation surface seems good and no sign of deterioration or decay is actually found. The same occurs even for irradiation with UV under ambient conditions.

Actually a systematic study is undertaken in order to have a deeper insight of the behavior of



this material under accelerated conditions of thermal ageing .

Reinforcement of Ancient Bones

This important material is found usually in advanced condition of deterioration and requires improvement for conservation/3/.

After four years of ageing under ambient conditions consolidated bones continue to show the same appearance. Even after many tens of hours under UV radiation and heating (30-40°C), no changes have been found. Accelerated sunlight ageing does not produce alterations after 46 days, corresponding to two years exposure under natural sunlight .

Reinforcement of Stones and Marbles

Stones and marbles have also been treated by gamma ray methods for conservation purposes. Our results are however very limited, due to difficulties of treatment for objects of big dimensions .

We have performed preliminary treatment of white and pink marbles with synthetic resins. Both types of marble show good improvement characteristics, but white marbles become slightly yellow when treated with styrene-polyester. No cracks have however been observed after treatment .

A type of soft stone has been treated with styrene-polyester (50⁰/o -50⁰/o) . Sometimes after consolidation (2-3 months) cracks of important extension appear. After four years of exposure to free atmospheric conditions, degradation seems to be faster than for untreated stone .

Concluding Remarks

The ageing behavior of consolidated materials by gamma rays, is still in the incipient period of degradation processes. It is however evident that durability and other properties of dry and waterlogged wood, of terracottas and bones are considerably improved. Efforts are necessary and more time is requested in order to have more reliable results.

Acknowledgements: The author is indebted to Mr A Antonopoulos and A Kokkinos for their assistance.

References

- /1/ E.G.Mavroyannakis: ICOM, 4th Triennial Meeting
Venice 1975/I8/2,3
- /2/ E.G.Mavroyannakis: ICOM, 5th Triennial Meeting
Zagreb 1978/I7/I
- /3/ E.G.Mavroyannakis: ICOM, 5th Triennial Meeting
Zagreb 1978/I7/2
- /4/ B.Detanger et ali: Int.Conf.Accademia dei Lincei
Rome-Venice 1973
- /5/ B.Detanger et ali: Int.Conf.Accademia dei Lincei
Rome-Venice 1973
- /6/ I.deNadaillac, R Cornuet:
Int.Conf.Accademia dei Lincei
Rome-Venice 1973
- /7/ G.Torraca:
Int.Conf.Accademia dei Lincei
Rome-Venice 1973
- /8/ J.de Jong:
ICOM, 5th Triennial Meeting
Zagreb 1978/7/I
- /9/ Anton Mihailov:
ICOM, 5th Triennial Meeting
Zagreb 1978/7/2 .

CONTROL OF CLIMATE AND LIGHTING

Coordinator: G. de Guichen (Italy)

Members : L. Bullock (UK)
 N.S.Brommelle (UK)
 R. Devina (USSR)
 R.L.Feller (USA)
 C. Kadijsky (Bulgaria)
 R. Lafontaine (Canada)
 K.J.Macleod (Canada)
 S. Miura (France)
 B. Ramer (UK)
 I. Rikuo (Japan)
 N. Stolow (Canada)
 E. Yoshimichi (Japan)

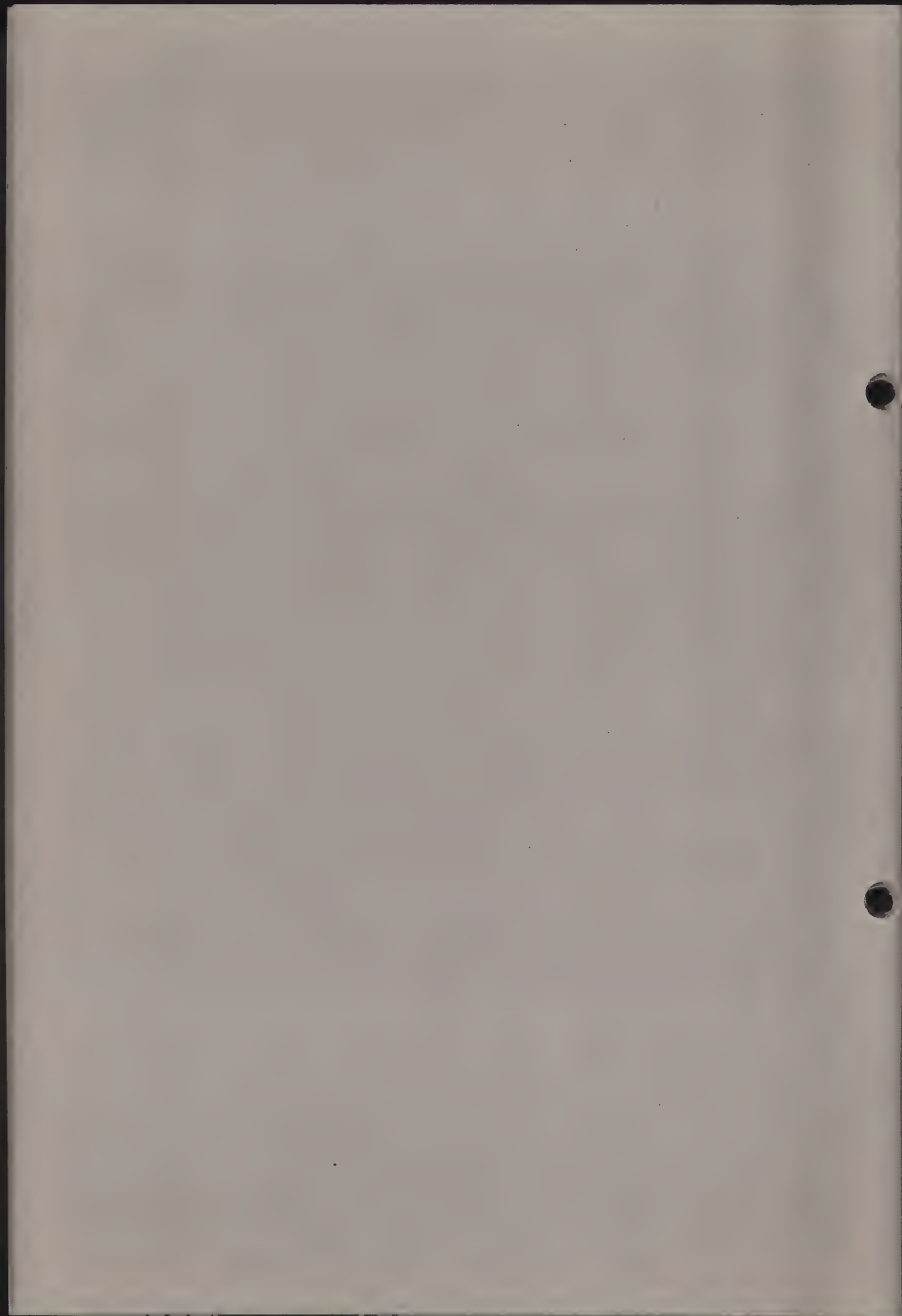
Programme 1978-1981

Climate

1. Collect information on producers of instruments measuring, registering, modifying climate and distribute it with possible comments from users (Kadijsky, Miura, de Guichen).
2. Make a study (of at least one year) of climate in a show-case, using different kinds of buffer agents (Ramer, Miura, Stolow, de Guichen).
3. Collect information on national climate standards in museums (if any) (Macleod, Kadijsky, Miura).
4. Development of microprobe for small spaces (Stolow).

Light

1. Collect information on special light sources and protective film, varnish, etc. Distribute this information with comments (Lafontaine, Bullock).
- Collect information on producers of measuring instruments (for visible and invisible radiation) (Feller, Bullock, Lafontaine).
3. Collect information on lighting standards (Feller, Macleod).
4. Aspects of visual perception (Brommelle).



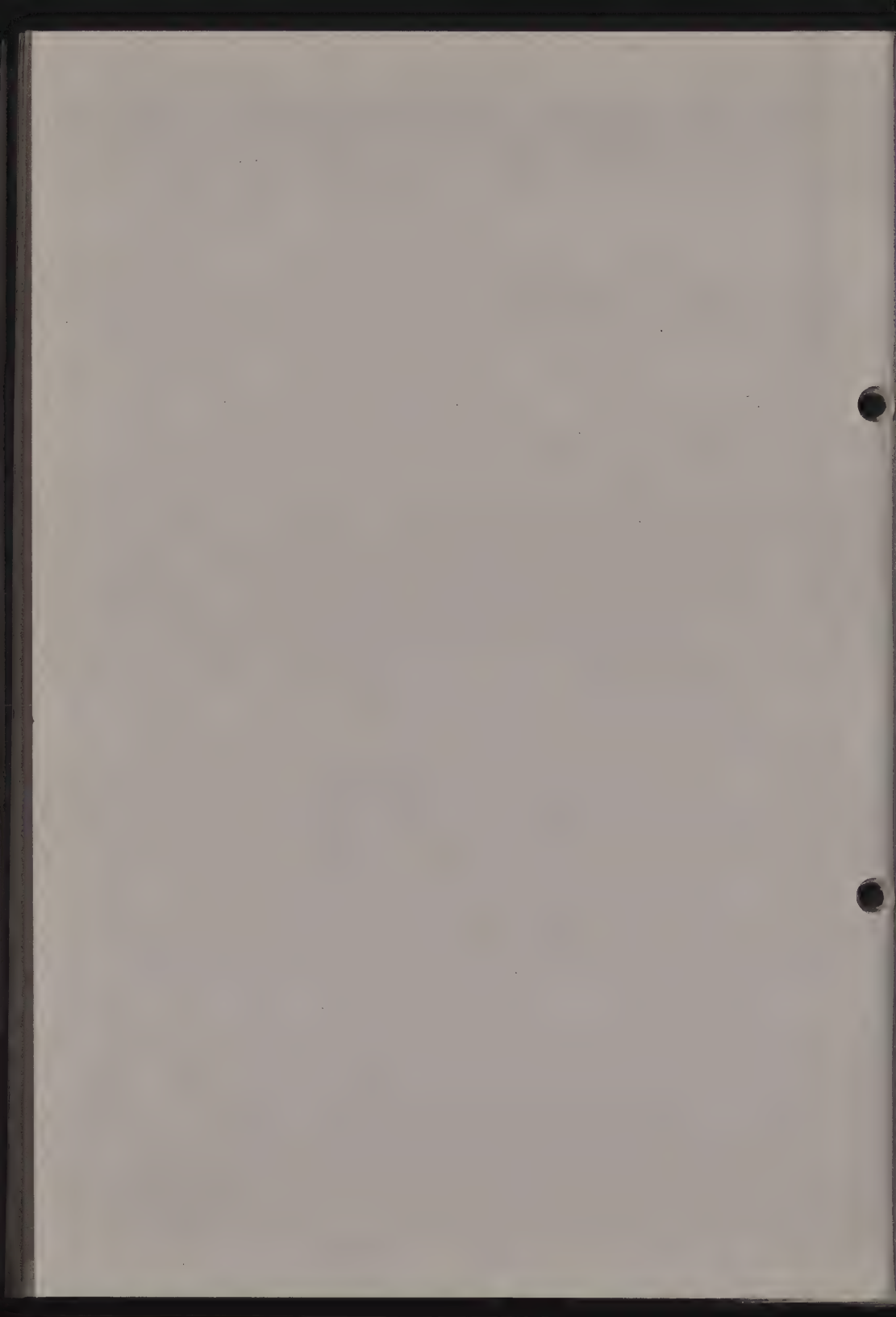
81/18/1

CONTINUED INVESTIGATIONS INVOLVING THE ISO
BLUE-WOOL STANDARDS OF EXPOSURE

Robert L. Feller and Ruth Johnston-Feller

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting



CONTINUED INVESTIGATIONS INVOLVING THE ISO BLUE-WOOL
STANDARDS OF EXPOSURE

Robert L. Feller and Ruth Johnston-Feller

Center on the Materials of the Artist and Conservator
Mellon Institute
Pittsburgh, Pa. 15213
USA

Abstract

Recent information regarding the International Standards Organization's (ISO) R105 blue-wool fading standards is reviewed, particularly the ways of instrumentally measuring their rate of fading and citations in the conservation literature of the proposed three classes of lightfastness based on ISO R105. A 1980 Japanese-American report on traveling exhibitions recommends that works that may contain colorants of the "fugitive" class be exhibited for no more than 5000 footcandle hours per year. The photochemically unstable character of seven traditional organic colorants, herewith reported, confirms the practical wisdom of this recommendation to limit the total annual exposure of certain materials. A lightfastness standard newly proposed in America, a purple polyester cloth, is noted.

Ways of Reporting Fading of ISO R105 Standards Under Various Conditions of Exposure

It will be recalled that at the Zagreb meeting, two sets of curves were published giving the rates of fading of the International Standards Organization's blue-wool fading standards (ISO R105) in terms of the changes in geometric-grey-scale contrast that occur during exposure in (a) an Atlas Electric Devices' carbon-arc fade-ometer with a Corex D filter, and (b) a 600WRC xenon-arc fade-ometer with pyrex/borosilicate glass filters.⁽¹⁾ At the previous meeting in Venice, four similar curves were given for exposures (a) on the wall of a gallery subjected to about 110,000-150,000 footcandle hours of diffuse daylight per year, (b) under an RS-type sunlamp, (c) under "daylight" fluorescent lamps, and (d) under glass outdoors facing south at Pittsburgh.⁽²⁾ This brings to six the number of graphs showing the rate of fading of the ISO blue-wool standards under various accelerated-aging conditions. Other laboratories may find that they will not be able to duplicate the graphs exactly. Nonetheless, these initial data provide useful guidelines on how fast one may expect the various blue-wool standards to

fade under widely different conditions.

It should be pointed out that the method used for plotting the rates of change in the blue-wool cloths - that is, plotting the logarithm of time against the geometric-grey-scale contrast (BS2662) with the assumption that the slopes are linear, although not necessarily parallel - is not a procedure described or officially recommended in the published ISO R105 standard.⁽³⁾ However, such graphs have proven to be of practical usefulness to others, as well as ourselves.^(4,5)

At the Zagreb meeting, the potential advantages of measuring the fading of the standards spectrophotometrically were discussed, either by measuring the luminous reflectance (the tristimulus Y value) or the reflectance at 620 nm (close to the point of maximum absorption). Instrumental methods of measurement were also the subject of a paper presented at the Toronto meeting of the American Institute for Conservation in 1979.⁽⁶⁾ In the Toronto paper, we discussed many of the same points that were presented at Zagreb but also referred to the use of various color-difference formulas for recording the fading of the standards, particularly the recent equation described by Vaeck.⁽⁷⁾ Our laboratory has not been satisfied with the use of ordinary color-difference calculations in lieu of measurements of the change in luminous reflectance (tristimulus Y value) or in reflectance at 620 nm. We have found that the latter two measurements provide reasonably linear relationships when plotted on log-log graph paper over a range of geometric-grey-scale contrasts from less than 4 to about 1. Graphical plots of color difference against time have traditionally not been considered to be linear much beyond a degree of fading corresponding to a grey-scale contrast of 4 or 3.⁽⁸⁾

Citations of Proposed Classes of Lightfastness

At the Venice and Zagreb meetings, the Center on the Materials of the Artist and Conservator proposed that three classes of photochemical stability be established on the basis of the ISO R105 blue-wool standards.⁽¹⁾ For convenience, this classification is reproduced in Table I. The table has been cited in at least two major publications since that date: in Garry Thomson's authoritative book on The Museum Environment⁽⁹⁾ and in a recently issued set of guidelines for traveling exhibitions drawn up by a joint Japanese and American committee.⁽¹⁰⁾

Suggested Standard of Total Annual Exposure for Class C Materials

The Japanese-American report contains a notable recommendation proposed as a standard for the total annual exposure for works that are known to contain or likely to contain "fugitive" materials of Class C character. The Japanese have had a long tradition of exposing many of their scroll paintings for only a brief period during each year. The suggested standard for Class C materials attempts to express the principle of this practice with greater precision: it is proposed that such materials be exposed to no more than 5000 footcandle hours (53,500 lux hours) per year.⁽¹⁰⁾ Although the type of illumination was not

specified, we would consider such a limitation to be particularly necessary if the spectral distribution of the source was similar in diffuse daylight or "daylight" fluorescent lamplight. This may be considered to be a source emitting an essentially continuous spectrum having a correlated color temperature about 5500 to 6500°K in which the total ultraviolet and visible irradiance would include about 3 to 7% near-ultraviolet radiation (320-400 nm). The temperature of the samples was about 26°C.

The intensity of the illumination is not specified in the recommendation. It is intended that 10 footcandles could be used for 500 hours of exhibition time, or 5 footcandles for 1000 hours. If a museum is open 8 hours per day, the latter arrangement would permit 125 days of exhibition per year. An intensity of 10 footcandles would allow for about 2 months of exhibition per year.

The reasoning behind this specification can be seen from consideration of the accompanying Figure 1, where it is indicated that ISO R105 standard No. 3 will fade to a grey-scale contrast of 3 in about 500,000 footcandle hours of exposure when the cloths are at a temperature of about 79°F (26°C) and are exposed in a room maintained at 50% RH. [In other words, 500,000 footcandle hours (about 5 million lux hours) is the approximate exposure to "daylight-like" illumination needed to appreciably fade a material of the "unstable" or "fugitive" photochemical class in Table I.] Thus, the recommendation, to expose objects for only 5000 footcandle hours per year, would permit about 100 years of exhibition before an amount of fading equivalent to geometric-grey-scale contrast of 3 would occur in a material of lightfastness class equivalent to the ISO R105 standard No. 3. When one realizes that materials equivalent to blue-wool standard No. 2 would fade to the same extent in half this time, the specification of 5000 footcandle hours per year should not seem unnecessarily restrictive. Padfield and Landi have shown that a considerable number of traditional textile dyes fall in ISO R105 Classes 1 and 2.⁽¹¹⁾ In Table II, we show that a number of traditional pigments also fall in similar ISO classifications.

Although the point is not made in the cited Japanese-American report⁽¹⁰⁾, it is fully appreciated that specification of irradiance in terms of footcandles will not clearly define the potential photochemical hazard. The spectral character of the light source used in testing or in a specification of lightfastness should be described, such as a "daylight" fluorescent lamp having a correlated color temperature of between 5500 and 6500°K; the percentage of near-ultraviolet radiation in relation to the total ultraviolet plus visible should be reported and some indication given of the conditions of temperature and humidity.

Another possible way of defining the character of the irradiance referred to when one has only a footcandle measurement to rely upon is to report the factor of damage per footcandle, D/f_0 , as calculated by Harrison.⁽¹²⁾ In the case of "daylight" fluorescent lamps, this would

be about 0.400 to 0.360 (D/f_c).

Purple Polyester Exposure Standard

The American Association of Textile Chemists and Colorists (AATCC) has recently been considering a new lightfastness standard based on a purple-dyed polyester cloth to replace the AATCC set of blue-wool standards.⁽¹³⁾ It may be recalled that the latter were not based on the same set of dyes as those used in the ISO R105 (BS1006:1971) cloths. The new standard intends to employ only the single purple-dyed fabric, which we have found to be approximately equivalent in rate of fading to the ISO R105 blue-wool No. 2. The Center at Mellon Institute will continue to investigate this potential new standard. However, because the degree of fading in the purple polyester must be measured instrumentally and is not intended to be rated by visual comparison with the geometric-grey scale, we cannot at the moment recommend the purple polyester cloth for general use by conservators. The ISO R105 blue wools still appear to be the most appropriate lightfastness standards to recommend to museum workers.

Fugitive Character of Several Traditional Colorants

Padfield and Landi rendered a great service to the field in reporting the relative lightfastness grades of a number of traditional textile dyes.⁽¹¹⁾ More than half of the dye-mordant combinations tested by these authors proved to be "fugitive" (equivalent to ISO R105 Class 3 or less). The Center on the Materials of the Artist and Conservator is currently measuring the lightfastness of a number of traditional fugitive pigments that can be encountered in various types of paintings (Table II). In particular, a recent investigation sponsored by Oberlin College with support of a grant from the National Endowment for the Arts enabled the Center to study the lightfastness of three colorants traditionally found in Japanese prints: indigo (ai), dayflower blue (aigami), and safflower red (beni).

The samples in Table II were usually tested as water-color washes on white rag water-color paper in which the wash had a luminous reflectance equivalent to Munsell value 5 to 7. Because the rate of fading of these organic colorants is likely to be sensitive to the relative humidity or to the "effective relative humidity" of samples that may be warmed by the high intensity of illumination, the lightfastness ratings in Table II must be considered as only approximate. If others attempt to duplicate their ratings, it may be found that they are reproducible only within ± 1 ISO R105 standard, particularly if other conditions of temperature, relative humidity and illumination are involved. Nevertheless, these tentative ratings strongly indicate that all are Class C materials, considerably more fugitive than the familiar and ubiquitous alizarin lake. It is understandable that restrictive recommendations for the total annual exposure are made for certain items in the collections such as Japanese prints, which are likely to contain colorants based on safflower, dayflower blue, carmine and indigo. Our investiga-

tions of the lightfastness of these and other organic colorants will continue.

References

1. Feller, R. L., "Further Studies on the International Blue-Wool Standards for Exposure to Light", Paper 78/18/2, ICOM Committee for Conservation, Fifth Triennial Meeting, Zagreb, 1978.
2. Feller, R. L., "Studies on Photochemical Deterioration", Paper 75/19/4, ICOM Committee for Conservation, Fourth Triennial Meeting, Venice, 1975.
3. ISO R105 is available as British Standard BS1006:1971 and as Schweizerischer Normen-Vereinigung SNV 95809-1961. The standard is said to be available also from Beuth-Vertriebs GmbH, Berlin and Köln and the Association pour la Détermination de la Solidité de Teintures sur Textiles, 12 rue d'Anjou, Paris, 8 me.
4. Jaekel, S. M.; Ward, C. D. and Hutchings, D. M., "Variations in Assessment of Lightfastness and in Rates of Fading and Spacing of the Blue Standards", J. Soc. Dyers & Colourists, 79 (1963), 702-722.
5. Feller, R. L. and Johnston-Feller, R. M., "Use of the International Blue-Wool Standards for Exposure to Light. I. Use as an Integrating Light Monitor for Illumination Under Museum Conditions", AIC Preprints of papers presented at the sixth annual meeting, Fort Worth, Texas, 1-4 June 1978, pp. 73-80.
6. Feller, R. L. and Johnston-Feller, R. M., "Use of the International Standards Organization's Blue-Wool Standards for Exposure to Light. II. Instrumental Measurement of Fading", AIC Preprints of papers presented at the seventh annual meeting, Toronto, Canada, 30-31 May and 1 June 1979, pp. 30-36.
7. Vaeck, S. V., "An Improved Color-Difference Formula for Use in Lightfastness Testing", J. Soc. Dyers & Colourists, 94 (1978), 301-306.
8. Berger, A. and Brockes, A., "Zur Beurteilung des Ausbleichens von Lichtechtheitstypen mit Farbdifferenzformeln", Die Farbe, 11 (1962), 263-274.
9. Thomson, G., The Museum Environment, London, Boston, Butterworths, 1978, p. 175.
10. Report of the Study Group on Care of Works of Art in Traveling Exhibitions of the Museum Exchange Subcommittee of the United States-Japan Conference on Cultural and Educational Interchange, Japan Society, 333 East 47th St., New York, NY 10017, 1980, p. 13 (cost \$1.50).
11. Padfield, T. and Landi, S., "The Light Fastness of the Natural Dyes", Studies in Conservation, 11 (1966), 181-193.
12. Harrison, L. S., Report on the Deteriorating Effects of Modern Light Sources, New York, The Metropolitan Museum of Art, 1954; see also Illum. Engr., 48 (1954), p. 253.

13. Babiarz, R. S. and Schuler, M. J., "A New Horizon in Lightfastness Testing", Textile Chemist and Colorist, 9, No. 3 (1977), 28-31.
14. Feller, R. L., "Standards of Exposure to Light", Bulletin American Group-IIC, 4, No. 1 (1963), 10-12.

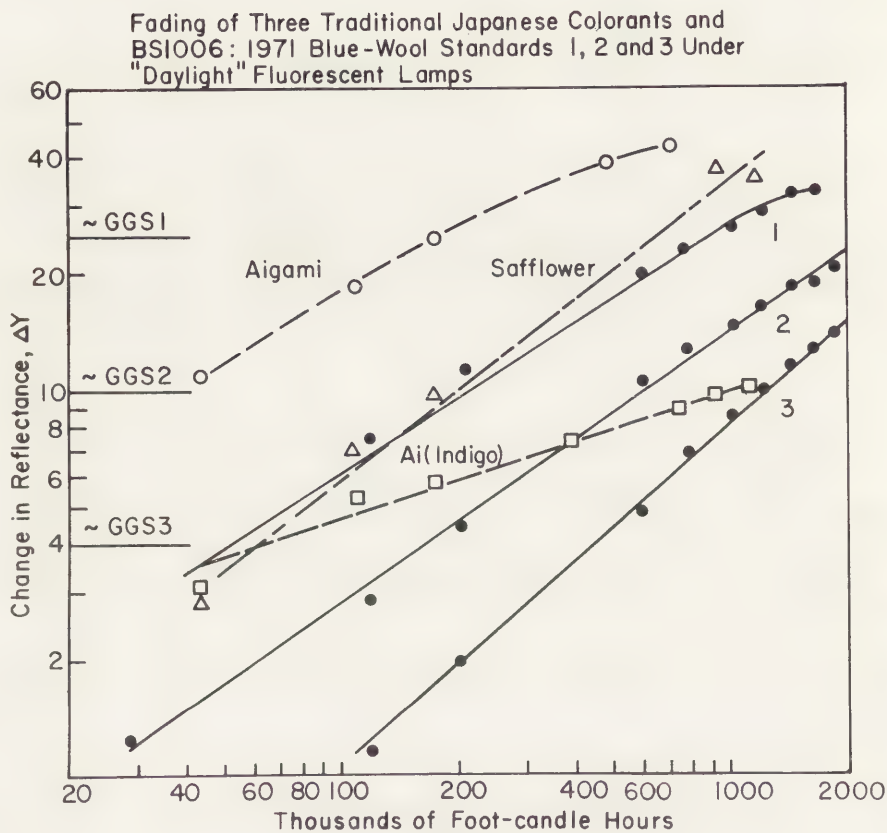


Figure 1

Table I

Proposed Standard Classifications of Photochemical
Stability for Materials in Conservation

<u>Class</u>	<u>Classification</u>	<u>Intended Useful Lifetime</u>	<u>Approximate Equivalent Standard of Photochemical Stability</u>
C	Unstable or Fugitive	less than 20 years	ISO R105 Class 3 or less
B	Intermediate	(20-100 years)	(Between Class 3 and 6)
A	Stable or Excellent	greater than 100 years	Greater than ISO R105 Class 6

Table II

Lightfastness of Some Traditional Pigments that are Fugitive
(Less Than or Equal to ISO R105 Blue-Cloth No. 3)

<u>Pigment</u>	<u>Approximate ISO R105 (or BS1006:1971) Lightfastness Grade</u>	<u>Reference</u>
Alizarin Lake (Control)	4 to 5	(14)
Indigo	2 to 3	this paper, Fig. 1
Quercitron Lake	2 to 3	(14)
Gamboge, Garcinia Morella	2 to 3	this paper, (14)
Carmin Lake (Carminic Acid Lake)	1 to 2	this paper, (14)
Safflower red, Carthamus		
Tinctorius (Benibana)	1	this paper, Fig. 1
Tumeric, Curcuma Longo	1	this paper
Dayflower blue, Commelina Communis (Aigami)	< 1	this paper, Fig. 1

Test exposures were made on samples placed 3 1/2" from General Electric H0 "daylight" fluorescent lamps in a room maintained at 21°C and 50% RH. Of the total irradiance between 320 and 700 nm, about 3.8% was determined to be in the near-ultraviolet (320-400 nm).



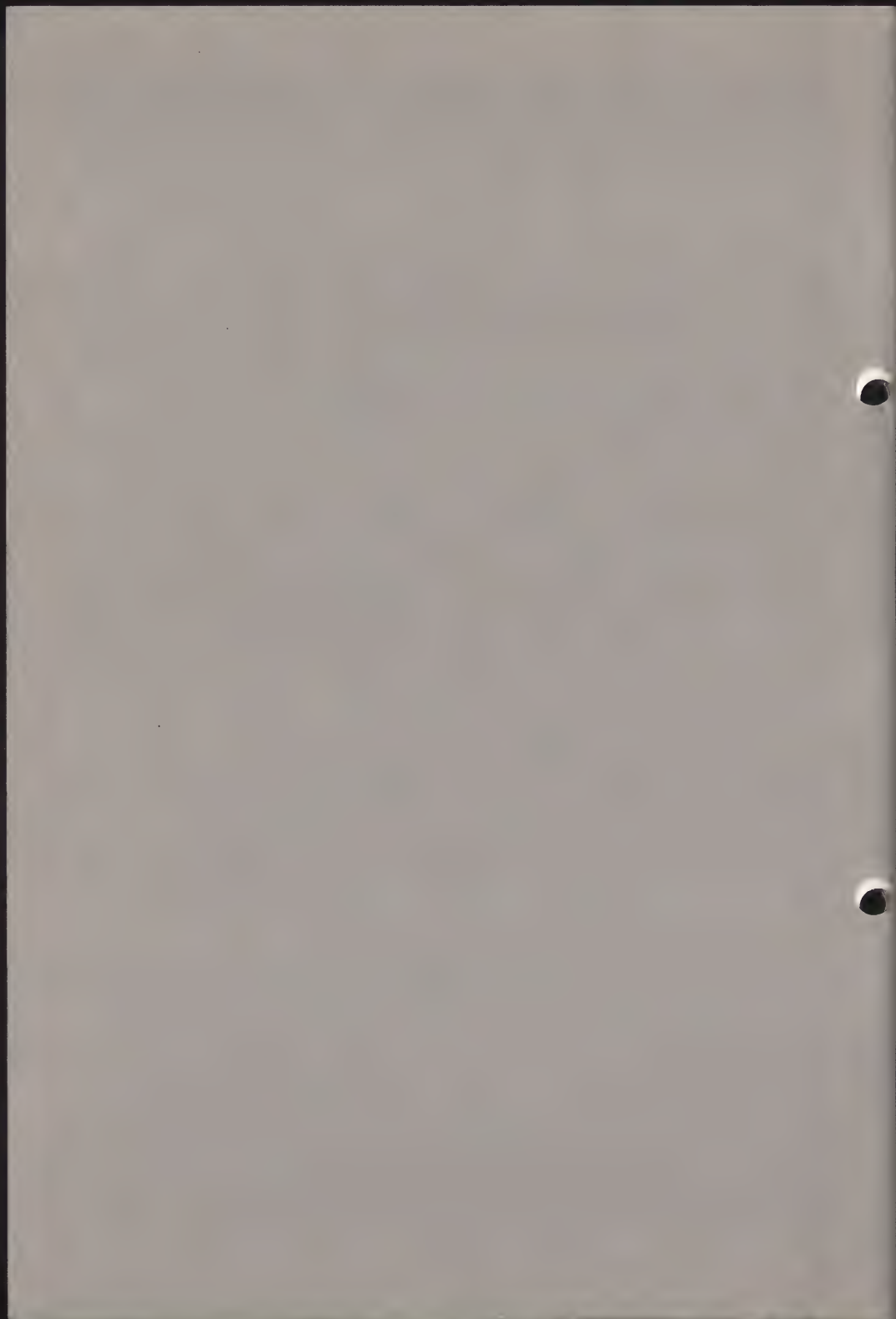
81/18/2

THE PRINCIPLE OF CREATING OPTIMAL LIGHTING
CONDITIONS IN MUSEUM EXPOSITION

S.G.Jurow, R.A.Devina and S.U.Zaichikova

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting



THE PRINCIPLE OF CREATING OPTIMAL LIGHTING CONDITIONS
IN MUSEUM EXPOSITION

S.G.Jurow, R.A.Devina and S.U.Zaichikova

WCNILKR

10 Khrestyanskaya pl

109172 Moscow

USSR

Summary

1. The relative coefficient of harmfulness (α) of light sources (lamps) produced in the USSR and used in museums has been evaluated. Its evaluation was made by Harrison's method (NBS, U.S.A.) and by the original method introduced in (RIR). (see Table 1).

2. A method of determining the quality of visual perception (QVP) of plane polychromatic exhibits has been developed; this method was employed by a group of experts (10-15 specialists), and each of them made 10-12 estimates of the variant of light conditions that was offered to him.

3. We have suggested the idea of optimal lighting conditions that should ensure the minimal optical harmfulness and at the same time give sufficiently good QVP of the exhibits.

The choice of optimal lighting conditions is made in practice by a group of experts; each of them should be informed about the harmfulness coefficients (see 1) of those kinds of lighting conditions which he is to observe. Guided by intuitive ideas about the desired and acceptable QVP of the particular exhibit, the expert chooses such lighting conditions that correspond to the normal ones by definition.

The same method is also used in selecting the optimal conditions when lighting devices (or windows) are supplied with light-protective filters removing u.v. and i.r. regions of the spectrum.

4. A series of experiments was made for choosing lighting conditions; they led to the conclusion that in displaying XVIII-XX century portraits painted in oil the optimal lighting conditions are ensured by incandescent lamps creating illuminance equal to about 75 lux.

For exhibiting Russian icons of XIX-XX centuries the optimal illuminance was found to be 50 lux; the same illuminance is also produced by incandescent lamps.

The term "optimal" is applied by us to conditions of light that ensure the minimal optical harmful effect of lighting (OHL) and sufficiently good quality of visual perception (QVP) of exhibits 1, 2.

The workers of the USSR Research Institute of Restoration (Ministry of Culture) studied and developed optimal methods of lighting plane polychromatic exhibits, but these methods can also be employed for lighting museum exhibits of any kind.

2. Optical harmfulness of lighting (OHL) is revealed as:

Direct photochemical destruction of molecules, obeying Bunsen-Roscoe principle;

Radiation heating, causing overdrying, deformation and cracking.

It will be recalled that according to Bunsen-Roscoe principle the quantity of the destroyed molecules is proportional to the quantity of photons hitting the substance.

The process of photochemical destruction of exhibits by the given light source can be quantitatively characterized as the rate of this process, which we shall call the dimensionless coefficient which shows how much quicker molecules are destroyed by one radiation, than by another one.

Table I, column \mathcal{L} (NBS) shows the values of \mathcal{L} calculated by NBS method (U.S.A.) (3) for various light sources used in the USSR to light museum exhibits. This calculation is based on the destruction of light-unresistant material (paper) by various radiations. Coefficient \mathcal{L} is used as a unit for incandescent lamps.

Table I

N	The light source	Colour temperature $T_{col.}$	The coefficient of destructiveness of radiation	
			According to Harrison method (NBS)	According to the method used by the USSR Research Institute of Restoration
1	The incandescent lamp	2850	1	1
2	The halogen incandescent lamp	3000	1.6	1.4
3	The luminescent lamp of warm white colour de lux	2700	1.7	1.6
4	The luminescent lamp of cold white colour de lux	3900	4.3	6
5	The luminescent lamp of cold white colour	4850	2.5	2
6	The luminescent lamp of daylight colour	6500	4.2	5.4
7	Natural light	6400	14	13

Another method of evaluation irrespective of the material has been suggested in the Research Institute of Restoration; it is based directly on Bunsen-Roscoe principle.

The essence of this method is simple if we know the spectra (in relative units) of radiations F_1 and F_2 which we compare; we choose the numerical values of

spectral intensities of each of them so, that light fluxes of these radiations (again in relative units) should be equal to:

(1)

After this we calculate the energy fluxes of radiation F_1 and F_2 in UV region from 300 nm to 400 nm.

(2)

We made calculations only for UV region, because it is this region that is the most active photochemically.

As the spectral region 300 nm - 400 nm is comparatively narrow, one can assume that the quantity of photons in it is proportional to radiation fluxes, hence,

(3)

The values of \angle estimated by the (RIR) are given in column \angle (RIR) in Table 1.

Close coincidence of numerical values of \angle calculated by both methods confirms the correctness of these values. Attention should be drawn to the fact that the values obtained by (RIR) are somewhat lower than \angle (NBS). The probable explanation is that the calculation made by the (RIR) method does not take into account photochemical destructions caused by photons in the visible region of the spectrum.

Studies of the optical harmful effect of visible light enable the researcher to suggest that when illumination changes N times, the rate of photochemical destruction (\angle) changes N times too, This dependence is of particular importance when one chooses optimal levels of illumination

(5)

Proceeding from energy considerations one can state that change in the illumination of exhibits results in the change of rate at which radiation damage occurs. But, methods of quantitative estimation of the rate of

radiation destructions have not been sufficiently popularized in museum practice.

3. The term "quality of visual perception" (QVP) is applied by us to the notion of aesthetic character, which synthesizes our intuitive and emotional ideas about the degree to which the appearance of objects is pleasing to the eye; this appearance depends on the distribution of brightness, colour rendering etc. It is clear that QVP may be better or worse, but there is no sense in asking the researcher to express numerically the degree of superiority of QVP under one kind of illumination over QVP under another kind of illumination! This means that the quantitative evaluation of QVP can be made only by the expert method in accordance with the scale of 5.4; this evaluation should be made with the help of some representative group of experts (GE).

To estimate QVP of works of art the group of experts should include:

museum curators

art critics

artists (painters), restorers

lighting technicians, working in the adjacent fields of engineering and art.

The quantitative evaluation of QVP of the particular (model 5) exhibit under various kinds of lighting is made by the expert who gives each of these kinds of lighting a certain number - a mark. In our experiments the experts used scales of three marks or five marks (fig. 1).

Fig. 1.

	-1	0	+1	
very bad	bad	indifferent	good	very good
-2	-1	0	+1	+2

The expert gave good or bad marks to QVP according to the following considerations:

It is natural to consider QVP normal if the light-

ing consitions reproduce those conditions under which the particular exhibit was made or for which the exhibit was intended. Thus, for example, the correct lighting conditions for exhibiting icons should admittedly be low illuminance levels (tens of lux) and low colour temperature (T_c) ($\approx 2000K$). For impressionists' landscapes the correct illuminance would be thousands of lux, and the normal colour temperature would be 6-10 thousand kelvins.

To evaluate QVP one may use a different approach. In some cases the experts can choose such lighting conditions which lend the exhibit greater "aesthetic value", make it "more beatiful". For instance, it is known that if icons are lighted by incandescent halogen lamps when illuminance is comparatively high, the QVP of these exhibits is considerably improved. These lighting conditions as distinct from normal ones may be termed "beautifying" conditions.

Of expecial interest to us are those cases when experts, wishing to lower OHL, choose lighting conditions with somewhat worse QVP in comparison with normal lighting conditions, and naturally, in comparison with beutifying ones.

For example, we consider it natural and advisable that impressionists' landscapes should be demonstrated under lighting conditions that are quite different from those that could be considered normal (see above).

Statistical processing of readings made by experts, when they estimated QVP, led to the conclusion that in order to obtain sufficiently correct results it is necessary to have (GE) of 10-15 experts, and each of them should make 8-12 readings which express the expert's opinion of QVP under the given conditions of lighting.

To estimate QVP one should make proper chcoice of exhibits which can be used as models when optimal light regimes are chosen.

But, choosing model exhibits, one should take into consideration the composition and the character of those exhibits, for which the optimization of lighting regime is carried out.

5. After all that has been said about the methods of estimating OHL and QVP, as well as about the choice of model exhibits, the principle and the practical ways of choosing the optimal e lighting regime for museum exhibits are in fact evident:

GE is offered several kinds of lighting model exhibits and is informed about the harmfulness coefficients \mathcal{L} of these kinds of lighting.

The experts are asked to choose lighting which ensures the minimal OHL and the QVP they consider suitable.

If GE chooses lighting with nonminimal OHL, then this can occur only if this kind of lighting, in the opinion of GE, ensures a substantially better QVP! It should be emphasized that in the numerous experiments in choosing optimal regimes, which were conducted in RIR and in the halls of Tretyakov gallery GE never selected any lighting conditions that were more harmful. This is explained by the fact that in all our experiments aimed at the optimization of light conditions for museum exhibits we used light sources which had already been practically approved in the museum lighting - incandescent lamps and luminescent lamps of various kinds. If we take a low pressure sodium-vapour lamp as an example, we may say without making any experiment that its spectrum (589 nm line) will be less harmful, than that of the incandescent lamp; again, a priori, we have no doubt that this lamp will be rejected due to its unsatisfactory quality of visual perception.

The tests for the optimization of light conditions, carried out in RIR, may be divided into two seri-

es: A and B.

In A series of experiments which were made at several levels of illuminance (50 and 100 lux) when pictures painted in tempera (icons) were illuminated, the researchers chose a light source (that is, the spectrum) which ensured the best and the most acceptable colour rendering. GE in which there were 10 experienced specialists (see 3) made a reliable decision to choose as the light source the luminescent lamp of cold white colour (de lux); made in the USSR; this lamp has colour temperature $T_c=3900K^*$ and ensured the best colour rendering when $E=100$ lux. But when the experts were informed that lamp the luminescent of cold white colour was much more harmful (see table 1) than the incandescent lamp, they unanimously preferred the incandescent lamp, though it gave worse colour rendering (that is, worse QVP) than the luminescent lamp of cold white colour. The incandescent lamp was chosen as the optimal source when illuminance was equal to 50 lux.

In B series of experiments, for several light sources (the same as those in A series) the researchers chose the best and the acceptable levels of illuminance when oil paintings were illuminated. Before the experts got to know the α , levels of illuminance of 75-150 lux were chosen as the most favourable. However, as soon as the experts got to know that the illuminance level of 75 lux will ensure the lowered rate of photochemical destruction of exhibits by about a factor of two; GE considered it possible to take this level (75 lux) as acceptable.

6. Special filters removing ultra-violet and infra-red regions of the spectrum begin to be used more

* The same result was obtained several years ago in the Institute of Technical Aesthetics during experiments with the faces of living people.

widely to reduce OHL. Selection of these filters organically belongs to the task of optimizing the light conditions, for they are selective in the visible region of the spectrum and hence somewhat change the chromaticity of visible radiation passing through them. The problem of choosing protective filters is practically solved in the same way as the above-mentioned choice of optimal lighting conditions. The experts are offered lighting conditions with filters and without them and they are told about the filter efficiency which shows by what factor the rate of deterioration in the exhibits is reduced with the aid of this filter. The expert estimates changes in QVP, caused by filters, selects filters which ensure maximal decrease of OHL and still acceptable QVP of the exhibits.

As a result of the work that was done, the sphere of application of light-protecting materials (mainly glass) in museums for fitting windows with glass and using cutoff in artificial light sources.

For using cutoff in incandescent lamps it is advisable to use heat-protective kinds of glass:

6.1. Heat-absorbing glass coloured in the mass.

6.2. Glass with oxide-lead-antimony coating.

For employing cutoff in luminescent lamps one can use.

6.3. Three-layered glass.

For employing cut-off of natural light in rooms containing exhibits and in storerooms glass of complex action, grey and bronzed can be used; its transmittance in the visible region is 40% to 75%.

In the course of our research we suggested a method of determining destruction ability of radiations irrespective of the material; using this method (RIR) as well as the method developed by Harrison (NBS), we made comparative estimates. The similarity of the resulting data obtained by various methods shows that

they are correct. In studying optimal parameters of the light medium in museum interiors we determined optimal light sources for illuminating nonlighting polychromatic objects (tempera). A member of experiments enabled us to establish the optimal source for tempera paintings (ikons) - the incandescent lamp of 50 lux.

It was also determined by the expert method, to what limits the levels of illuminance on oil paintings, which are accessible to perception, could be lowered when various light sources are used. When the luminescent of cold white colour lamp is used, illuminance could be lowered to 80-90 lux; when the incandescent lamp is used, illuminance can be lowered to 75 lux. Lighting conditions created by the incandescent lamp when illuminance is 75 lux are considered to be optimal. We examined also several kinds of glass and after making estimations and experimenting we determined the sphere of their applications in museums.

In conclusion we shall give some recommendations concerning the problems of optimizing lighting conditions in museum interiors:

Optimization of lighting conditions for museum exhibits should ensure lowering to a possible minimum optical harmfulness caused by lighting and at the same time it should ensure the sufficiently good quality of visual perception of exhibits.

Optimization of light conditions should be based on the expert judgement of QVP of model exhibits and at the same time on the due consideration for harmfulness coefficients of these kinds of lighting conditions which were compared.

Great diversity of exhibits (works of art) and museum interiors in which they are displayed makes the creation of common lighting conditions impossible. Hence, it is impossible to come to the same decision concerning in particular the level of illuminance. The abo-

ve-mentioned admissible illuminance levels (50 lux and 75 lux) and the admissible light source - incandescent lamps - should be regarded as the averaged orienting points.

As the main task of every museum is storage of exhibits for as long a time as possible, the main task of lighting optimization lies in choosing the minimum possible value of optical harmfulness. The choice of the variant having higher optical harmfulness can be made only for the sake of considerable gain in the quality of visual perception. The necessity of this choice should be substantiated by the averaged opinion of the group of experts, and each of them should know the coefficients of relative optical harmfulness of these variants when he estimates their QVP.

Reference

1. On the principles of optimization of lighting conditions for museum exhibits. "Svetotekhnika", N 11, 1976.

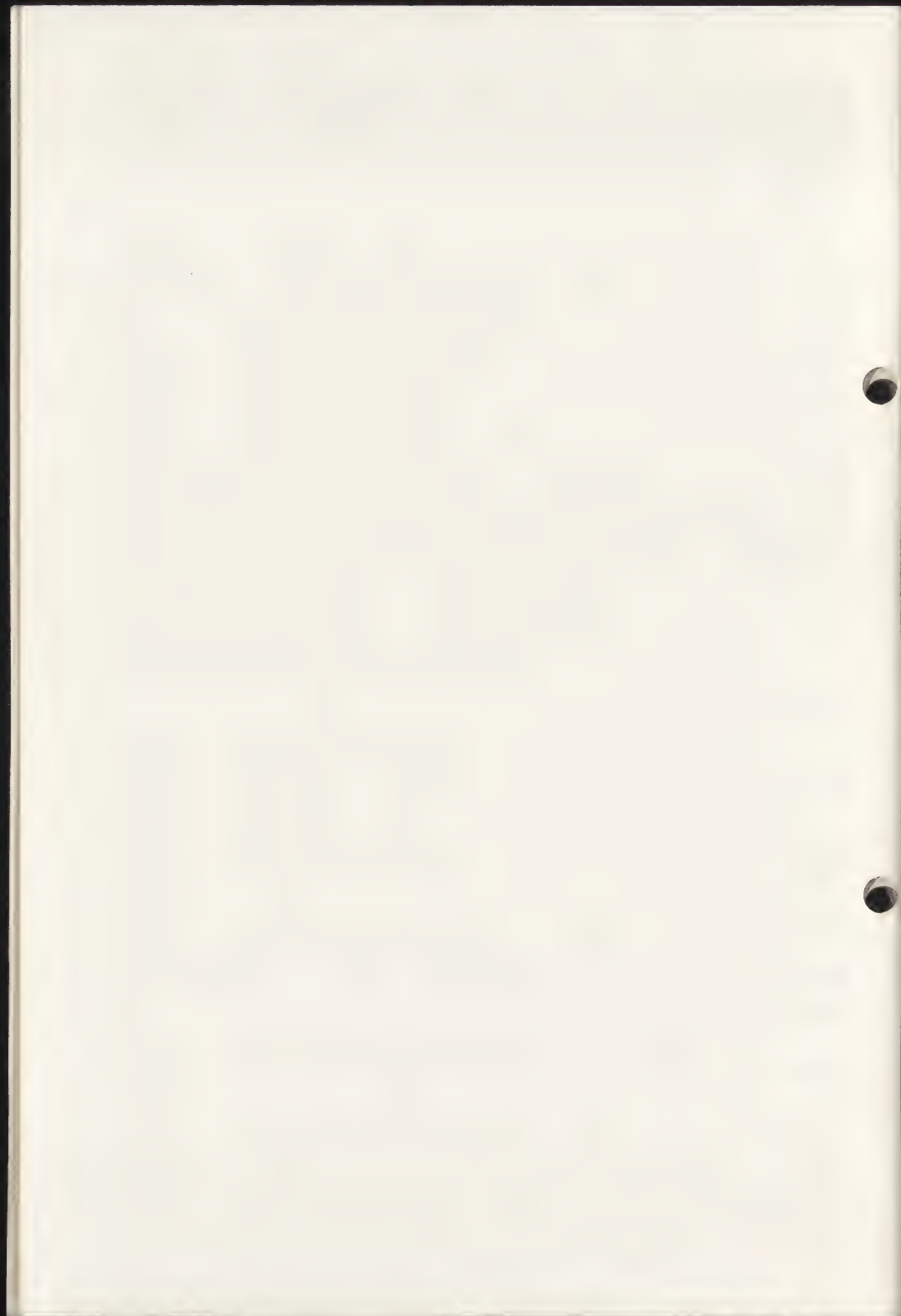
Jurov S.G., Gorin I.P., Devina R.A., Ershov U.A., Zaichikova S.U.

2. The choice of optimal conditions for lighting museums. "Khudozestvennoe nasledye", N 34, 1978.

Jurov S.G., Gorin I.P., Devina R.A., Ershov U.A., Zaichikova S.U.

3. Harrison L.S. Report on the deterioration effects of modern light sources, The Metropolitan Museum of Art, New York, 1954.

4. Ivanova N.S. and others. Subjective estimation of colour rendering R.I.T.A., 1973.



81/18/3

ON TEMPORARY EXHIBITIONS

Roberto Nardi

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting

ON TEMPORARY EXHIBITIONS

Roberto Nardi

Via Zanardelli 16

00186 Roma

Italy

SUMMARY

Objects shown in temporary exhibitions are subject to damage caused by abrupt changes in temperature, and even the more so by change in the relative humidity. Under these circumstances the changes in the atmosphere are rendered particularly sudden by the heavy and irregular influx of visitors and the unusual dimensions of the rooms. This study is based on data from two hygro-thermographs operated from the 15th to the 29th of december 1980 during the exhibition of 43 works by Kandinsky held in Rome at the Capitoline Museum from the 12th of november 1980 to the 4th of january 1981. The data provided by the instruments, one inside and one outside of temporary wooden structure of the exposition, bear on three aspects of the problem:

- 1) The effect of wooden walls on variations in the microclimate
- 2) The number of visitors and the rythm of their arrival
- 3) The volume of exhibition space and the number of works exposed.

.....

Because of their exceptional character, temporary exhibitions present the best opportunity to study the changes in temperature and relative humidity which, although always present in museums, are particularly evident in this type of show.

Sudden changes in relative humidity are well known to be harmful to the works displayed because of their influence on the organic materials of which they are composed; in the past, much damage has been done to objects exhibited in this fashion.

By 'exceptional' I refer to variable parameters such as the volume of the exhibition spaces, the number of visitors and the rythm of their arrival, as well as the number of works exposed.

It is the effect of these variables that we can read on the hygro-

thermograph, translated in terms of variations in temperature and relative humidity.

The readings were taken at an exhibition of 43 works by Kandinsky, comprising oil paintings on wood and canvas, and watercolours on paper.

The show was held in a room of the Capitoline Museum in Rome from the 12th of november 1980 to the 4th of january 1981.

The particular structure of the exhibition space permitted a study and quantification of the effect of wooden partitions on modifications in the microclimate.

The room in which the exhibition was held (Room VI of the Capitol Pinacothecae) measures 10 x 21,20 metres, and is 7 to 8 metres high with a vaulted ceiling. There are thus 212 square metres of floor space and a volume of approximately 1590 cubic metres.

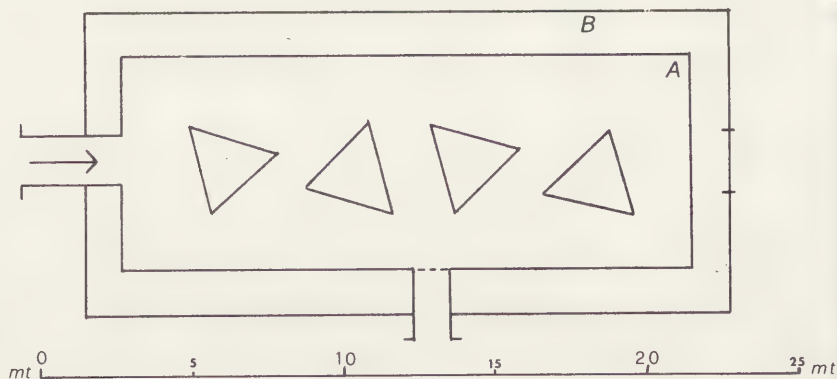
Inside this room was constructed the exhibition area, a rectangular pavillion with the walls and floor built of wood panels 8,5 centimetres thick, and the ceiling of cloth. The space thus formed measured 7,20 by 19,20 by 3,85 metres, with a floor space of 138,50 square metres and a volume of 525 cubic metres.

Between the walls of the room and the temporary structure was thus created an air space of around 1,5 metres.

Inside the exhibition space were four triangular elements, 3 metres on a side and 3 metres high, constructed of wood and cloth.

This contained the lighting system, conditioned the circulation in the room and supported some of the pictures.

PLANT (approx.)



Two hygro-thermographs were placed in the room, one inside the pavillion and one outside. These functioned between the 15 and the 29 of december, including the three days during which the exhibition was closed.

It was thus possible to register on the first instrument (A) the climatic modifications in the interior of the pavillion, in immediate contact with the works exposed, and on the second (B) the data as modified by the wooden walls.

As the visitors to the exhibition represent the determining factor for the climatic modifications, the variation between the two instruments takes on an internal-external aspect.

The climatic changes outside the building itself are not considered, as these have an equal weight on both instruments.

The first diagram is that of the data from instrument (A).

The bottom graph shows the maximum and minimum of the temperature and relative humidity in the space of each 24 hours period and, most important, the time passed between the two values: the time employed by the peaks in order to reach their maximum extension.

The upper graph shows the number of visitors daily.

We can immediately perceive the rather undisciplined behaviour of the public, with the greatest influx on Saturdays and the smallest on the 24th of december, during the last-minute Christmas shopping.

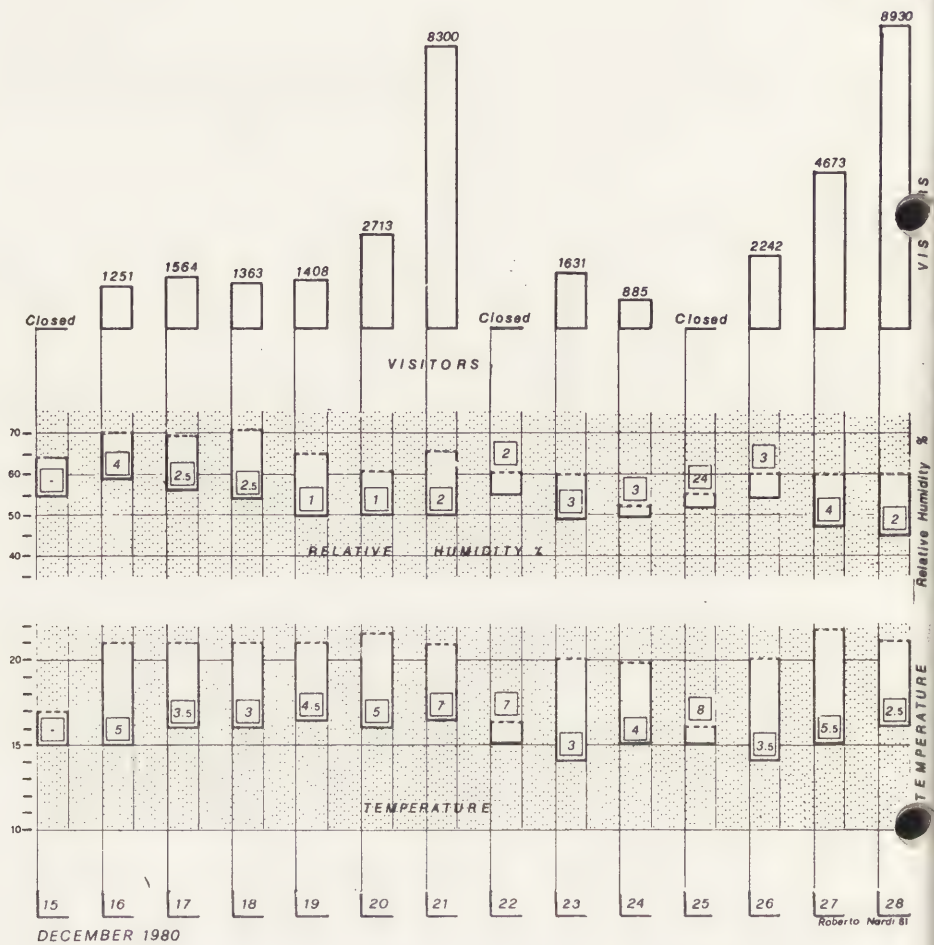
Putting the two sets of data together we can see the relationship between the number of visitors and modifications in the microclimate, in particular, the jumps in relative humidity which are so dangerous to the works exposed.

In the second diagram the data from instrument (A) is compared with that from instrument (B).

In the upper part the changes in temperature and relative humidity from (A) are shown in broken line, those from (B) in a continuous line.

In the lower part the quantity of those changes, expressed in degrees centigrades and % of relative humidity are compared for the two instruments.

The analysis of the data shows that while the two instruments measure conditions which are directly related, those from (B) are cushioned in that, with the single exception of relative humidity on the 16th,



----- Maximum daily values

_____ Minimum daily values

xh Time employed in order to reach min. & max. values

Diagram 1

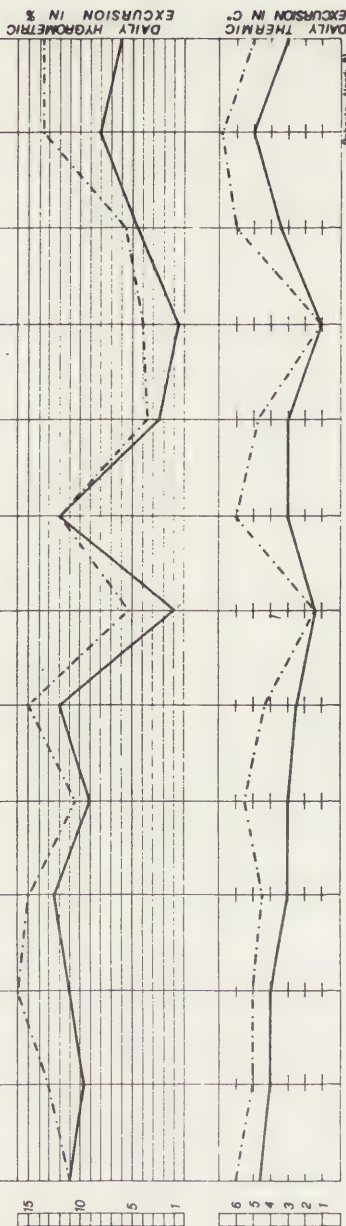
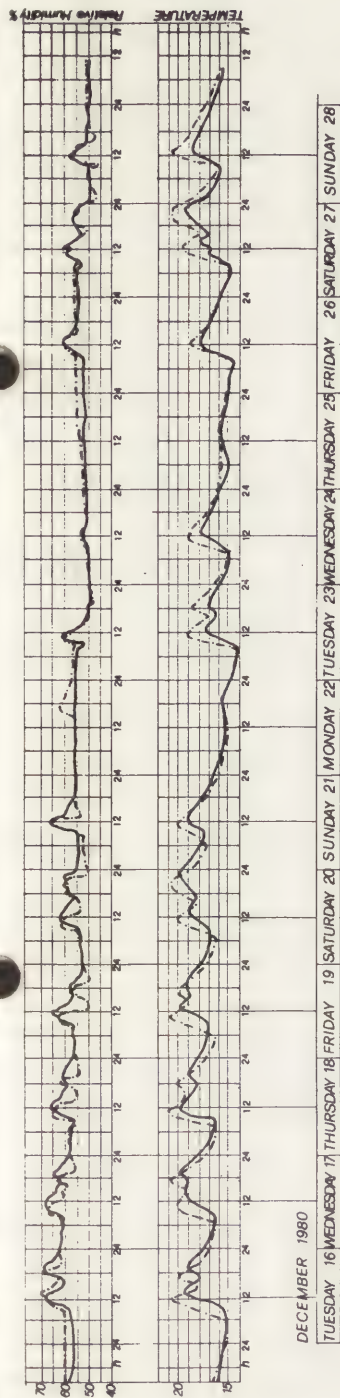


Diagram 2

they are always lower than the (A) values.

...

It seems unnecessary to underline the damage provoked by the shock of the sharp changes in the relative humidity on the works, and the frequency with which these shocks take place in this sort of exhibitions.

The show studied was not an isolated or particularly egregious example; indeed, it is perhaps one of the least 'tragic'.

Before turning to three simple actions that could be taken to modify these effects I would like to note that I have not considered the possibility of installing direct climatic modifiers - humidifiers, dehumidifiers, heating or air conditioning - in the exhibition space, first, because I do not consider these simple solutions and second because my analysis presupposed that expensive appliances were absent or impossible.

1) — The first idea is based on the second graph with which we can observe the behaviour of the wooden partition as a buffer.

On average, the cushioning effect is around two to four points for relative humidity and one to three points for temperature.

The time taken to achieve the peak levels is slowed by two hours.

Two hours are of course still too abrupt a change for variations of relative humidity of this magnitude.

But even some slowing down together with a slowing of the limiting values, would be a worthwhile result.

These effects can be seen to be important when we consider that the modifications run around 10 to 15 points for relative humidity and 4 to 6 points for temperature.

It is worth noting that on the days in which the exhibit was closed (22nd, 25th) and on the 24th, with the minimum attendance of 885, the relative humidity line on instrument (B) remains constant even though that of (A) shows a steady, although slight, rise.

One should note that small modifications such as the elimination of draughts and sudden gusts of air, easily obtainable without air conditioning, would greatly modify the results obtained in this study.

All this leads me to propose that the works of art be displayed outside a wooden pavilion, constructed with glass panels to permit the viewing of the objects from within while avoiding direct contact between

two spaces.

Although I admit that this leads us directly to the 'glass or no glass' debate.

- 2) — My second proposal bears on the direct cause of the abrupt climatic changes, that is to limit the number of visitors and avoid abrupt changes in the influx of visitors.

Observing the data from the first diagram, with particular attention to the relative humidity, we can see that 1000 could be a good value.

Comparison between the results from the 18th, with 1363 visitors, and those from the 22nd and 25th, when the exhibition was closed and Christmas eve, when the minimum of 885 visitors occurred, makes this point clearly.

If one considers the weekly average such an adjustment does not seem particularly brutal, while the elimination of the early afternoon closure would avoid the temporary changes which cause the most harm.

- 3) — A third possibility, more an intuitive judgement because I do not have at my disposition specific data with which to make a comparison, is to modify the exhibition space or, better, to increase the proportion between the volume of the space and the number of works displayed.

And therefore the same increase in cubic metres of air, if we double the exposition surface; major distribution of visitors, if we divide the works in several exposition areas, could have a notable effect, I suppose, a thus proving a much wider range in buffering the climatic variations.

81/18/4

STUDIES ON THE BEHAVIOR OF RH WITHIN AN
EXHIBITION CASE. PART I: MEASURING THE
EFFECTIVENESS OF SORBENTS FOR USE IN AN
ENCLOSED SHOWCASE

S. Weintraub

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting

STUDIES ON THE BEHAVIOR OF RH WITHIN AN EXHIBITION CASE.
PART I: MEASURING THE EFFECTIVENESS OF SORBENTS FOR USE
IN AN ENCLOSED SHOWCASE

S. Weintraub

Objects Conservation
Metropolitan Museum of Art
82 Street and 5th Ave
New York, NY 10028
USA

ABSTRACT

The limitations of sorbents presently used in conservation to buffer changes in RH within an enclosed showcase suggest the need for more efficient buffering materials. Concepts that can be used to estimate the efficiency of different sorbents form the subject of this paper. 'M values' are used to express the buffering capacity of a sorbent within a 'designated RH range'. The hysteresis of a sorbent is accounted for by using a positive value for adsorption and a negative value for desorption. The actual significance of hysteresis on a sorbent within a designated RH range is discussed, and 'designated M+ values' or DM+ values are introduced in order to summarize the actual buffering capacity of a sorbent which exhibits hysteresis within a designated RH range. Four different types of silica gel and Nikkapellet are analyzed to illustrate the use of the above mentioned concepts.

INTRODUCTION

The ability to control relative humidity within a showcase with a non-mechanical system is accomplished by means of a moisture sensitive material, referred to as a sorbent, that can buffer changes in relative humidity (RH). Because of high adsorption capacity, good response time, temperature independence, and low cost, regular density silica gel has been preferred over other sorbents as an excellent case buffering material. A related type of material, Nikkapellet, has been used in Japan for the same purpose. However, there are other types of silica gel and related sorbents which also may be used to buffer changes in RH. The purpose of this report is not to recommend any specific type of sorbent, but rather to suggest a number of concepts that can be used in comparing

the efficiency and appropriateness of different sorbents for use in stabilizing the relative humidity within a showcase.

TYPES OF SILICA GEL

The physical characteristics of silica gel can vary considerably, depending on the technique employed in their manufacture. In fact, only a limited number of silica gel types are available, chosen because of their suitability for general industrial needs. Four types of silica gel, as well as Nikkapellet, were chosen for examination in this report on the basis of the wide variation between each type in their moisture content/relative humidity (MC/RH) relationship, i.e. the amount of moisture contained by the sorbent at a particular RH.

1. Regular Density Silica Gel (W.R. Grace and Co., Davison Chemical Division, Baltimore, Maryland 21203, U.S.A.): The MC/RH curve used to represent this gel is fairly typical of most regular density silica gels available commercially. This type of gel is distinguished by its very high adsorption capacity below 50% RH and its rather low adsorption capacity above 50% RH.
2. Nikkapellet (Nippon Kasseihakudo Co., Ltd., 1, Kanda-hirakawa-cho, Chiyoda-ku, Tokyo, 101, Japan): Nikkapellet is manufactured from a Montmorillonite clay which has been treated with sulfuric acid, and washed with sodium silicate to impregnate the clay with silica gel.
3. Intermediate Density 59 Silica Gel (W.R. Grace and Co., Davison Chemical Division): Intermediate density silica gel has a higher adsorption capacity than regular density silica gel. It is distinguished by its low moisture adsorption capacity below 70% RH and its very high capacity as it approaches 100% RH.
4. B Type Gel (Fuji-Davison Chemical, Ltd., 1846 2-chome, Kozoji-cho, Kasugai-shi, Aichi-Ken, Japan 487): This is also an intermediate density type of silica gel, similar to ID 59. It begins to exhibit a large increase in adsorption capacity around 60% RH.
5. Silica Gel III: This is a new experimental type of gel and is not available commercially. It is included in this report in order to demonstrate the wide variety of properties that different types of silica gel can have. This gel is similar to regular density silica gel in its relatively high moisture content below 50% RH, while above 50% RH it behaves like an intermediate density gel because of its rapid increase in adsorption capacity.

The statistical description of the MC/RH curves used in this report are derived from the author's tests (between 40-70% RH) and company data. Because of the large variation in the MC/RH curve for different batches of the same gel type from the same manufacturer, the information included here can only be used as an approximate model of a typical MC/RH curve, not an exact representation of any specific silica gel. Before any specific batch of silica gel is used, it is important to test the batch and determine its particular MC/RH relationship.

THE MOISTURE CONTENT/RELATIVE HUMIDITY RELATIONSHIP

Generally, the utility of a sorbent is measured by its overall MC/RH relationship. Such curves (fig. 1) show the moisture capacity of a material throughout the entire humidity range. In fact, only a small part of the RH range, referred to here as the designated RH range, is used when exhibiting moisture sensitive objects in an enclosed showcase. Because it may not be readily apparent from these general MC/RH curves which silica gel is most appropriate for any given designated RH range, it is helpful to examine the change in moisture content within the designated RH range desired for a specific exhibition show case. For example, assume that the RH within the case is allowed to

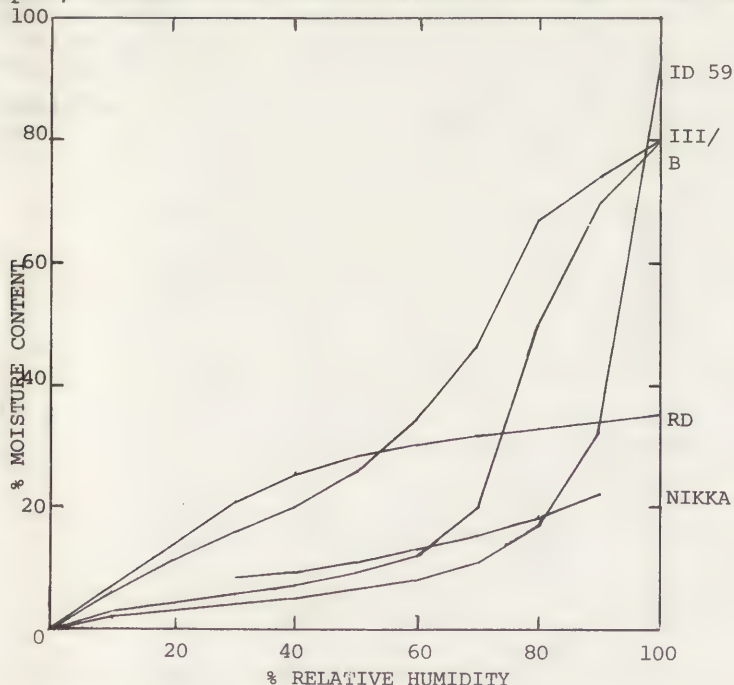


FIGURE 1 MOISTURE CONTENT/RELATIVE HUMIDITY PLOT FOR FIVE SORBENTS

vary between 40-60%; when it exceeds these limits, the sorbent is reconditioned. Under these circumstances, the predetermined 40-60% RH range is the 'designated RH range' and it is the moisture content specific to this range which becomes important in estimating the efficiency of a sorbent.

Chart 1 presents the absolute moisture content for the five types of gel at 10% RH intervals. The number given in parentheses is the difference in moisture content at each interval. This number also can represent the average 'M value' or 'specific moisture reservoir', a concept introduced by Thomson¹, where the M value represents the amount of water in grams that is gained or lost by one kilogram of a sorbent when the RH changes by 1%. A high M value indicates a high buffering efficiency, i.e. a large amount of moisture capacity is available to buffer changes in RH.

The efficiency of a sorbent also can be represented graphically by plotting the incremental sum of M values within a specific designated RH range, using the beginning of the designated RH range as the zero-point. Figure 2 represents such plots within a designated range of 40-70% and 50-70% RH. These graphs clearly illustrate that despite the high overall moisture content of regular density silica gel in the 40-70% and 50-70% RH range, its useful moisture reservoir capacity in both designated RH ranges is extremely limited. In contrast, ID 59 gel, with a very low capacity, is actually a more efficient buffer between

CHART 1 The Moisture Content for Five Sorbents from 0-100% RH

% RH	RD	NIKKA	ID 59	B TYPE	III
0	0	-	0	0	0
	(7.0)		(2.0)	(2.5)	(6.5)
10	7.0	-	2.0	2.5	6.5
	(7.0)		(1.0)	(1.5)	(5.0)
20	14.0	-	3.0	4.0	11.5
	(6.5)		(1.0)	(1.5)	(4.5)
30	20.5	8.5	4.0	5.5	16.0
	(4.5)	(1.0)	(1.0)	(1.5)	(4.0)
40	25.0	9.5	5.0	7.0	20.0
	(3.5)	(1.5)	(1.5)	(2.0)	(6.0)
50	28.5	11.0	6.5	9.0	26.0
	(2.0)	(2.0)	(1.5)	(3.0)	(8.5)
60	30.5	13.0	8.0	12.0	34.5
	(1.5)	(2.5)	(3.0)	(8.0)	(12.5)
70	32.0	15.5	11.0	20.0	47.0
	(1.0)	(3.0)	(6.0)	(30.0)	(20.5)
80	33.0	18.5	17.0	50.0	67.5
	(1.0)	(4.0)	(15.5)	(20.0)	(6.5)
90	34.0	22.5	32.5	70.0	74.0
	(1.0)		(61.0)	(10.0)	(6.0)
100	35.0	-	93.5	80.0	80.0

50 and 70% RH. Similarly, in spite of the low moisture content of B type gel, the sharp increase in its M value above 60% makes it a very effective buffer at higher levels of RH. While the very high efficiency of III type gel can be assumed from figure 1, figure 2 illustrates that it is about two times as effective as B type gel, and about four times as effective as the remaining gels between 40-70%, about five times as effective between 50-70% RH.

The utility of M values in determining the effectiveness of silica gel can also be demonstrated by actually estimating the buffering effect of silica gel at a specific RH. For example, the addition of 15 grams of water to an enclosed space containing one kilogram of buffer will cause the following theoretical changes in RH within the case (determined by dividing the amount of water added by the specific M value):

	M Value	40% RH		M Value	60% RH	
		Change in RH	Final RH		Change in RH	Final RH
RD	3.5	4.3	44.3	1.5	10.0	70.0
NIKKA	1.5	10.0	50.0	2.5	6.0	66.0
ID 59	1.5	10.0	50.0	3.0	5.0	65.0
B TYPE	2.0	7.5	47.5	8.0	1.9	61.9
III	6.0	2.5	42.5	12.5	1.2	61.2

At 60% RH, a list rank ordering the five types of gel from highest to lowest according to their overall moisture content and ability to minimize changes in RH are shown below:

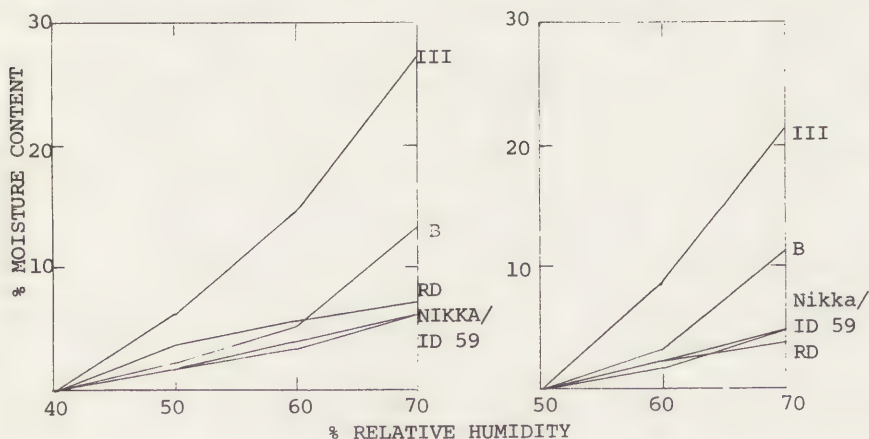


FIGURE 2 MC/RH Plot within the 40-70% Designated RH Range and 50-70% Designated RH Range

Overall Moisture Content

1. III type
2. Regular Density
3. Nikkapellet
4. B type
5. ID 59

Effectiveness

1. III type
2. B type
3. ID 59
4. Nikkapellet
5. Regular Density

Such a listing shows that there is no direct relationship between the actual moisture content of a particular sorbent and its relative ability to control the RH of a showcase. Therefore, in judging the utility of a sorbent for use in stabilizing RH, it is critical to examine its behavior within the designated RH range. The effectiveness of a sorbent within this designated RH range can be demonstrated by 1) its M value, 2) a graph plotting the sum of M values within a designated RH range, and 3) actually estimating the buffering effect at a particular RH for a given addition of water to the showcase.

HYSTERESIS

Many sorbents have an adsorption curve which is slightly different from, and lies below the desorption curve; this phenomenon is called hysteresis and the zone between the two different curves is the hysteresis loop. The MC/RH curves for the five types of gel discussed in the previous section were based only on the adsorption curves and do not take the desorption curves into account. Since the slope and, therefore, the M value of the desorption curve differs from the adsorption curve, the actual moisture reservoir capacity of a given sorbent will depend upon whether the gel is desorbing or adsorbing as well as its designated RH range. This can be indicated by making the M value positive for adsorption and negative for desorption.

The determination of the exact M value is further complicated when the sorbent begins to desorb before it has reached the point of convergence between adsorption and desorption. This will result in an intermediate MC/RH curve which can occur anywhere within the hysteresis loop. Figure 3 illustrates a simplified hysteresis loop with three different intermediate desorption curves beginning from Point A on the adsorption curve. Within the 40-60% RH range, both the outer adsorption and desorption curves have an M value of 5, whereas internal desorption curves AB, AC, and AD show M values of 0, 2.9, and 5 respectively. Investigations² indicate that intermediate adsorption-desorption curves occurring within the hysteresis loop will only gradually reach the far edge of the loop. Also, the slope of the intermediate adsorption or desorption curve will be somewhat parallel to the general adsorption or desorption curve, except at the points of divergence and convergence, where it will flatten out. Thus, the slope of such an intermediate curve is more likely to resemble

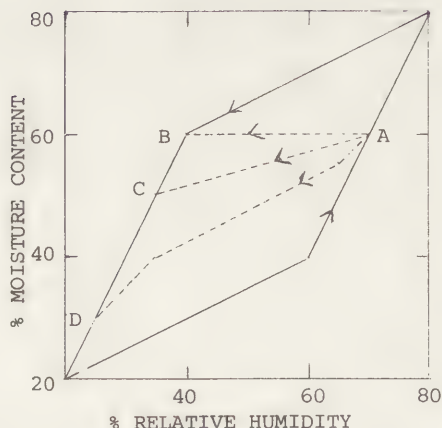


FIGURE 3 Theoretical MC/RH Plot for Hysteresis

AD than AB in figure 3. An intermediate adsorption curve will trace a similar path.

The flattening effect at the terminal zones of the intermediate MC/RH curve within the hysteresis loop will result in an average M value for the intermediate adsorption or desorption MC/RH curve similar to but somewhat less than the general adsorption or desorption MC/RH curve. Furthermore, these intermediate MC/RH curves will describe a new hysteresis loop within the designated RH range; the M values within this new hysteresis loop, called the designated hysteresis loop, indicate the actual effectiveness of a sorbent within a specific designated RH range (see descriptive examples below). These new M values can be expressed as the 'designated M values' or DM values. Any intermediate MC/RH curve within this designated hysteresis loop can be expected to have a DM value similar to but slightly less than the general DM value.

In summary, the M value indicates the overall moisture content available to buffer changes in RH. These values are based on the MC/RH curves over the entire 0-100% RH range. A positive M value represents the adsorption curve, a negative M value, the desorption curve. The DM value indicates the moisture content available to buffer changes in RH only within the designated RH range. Thus, the characteristic efficiency of a sorbent under real conditions can be represented quite accurately and succinctly by its DM \pm values.

The general and designated hysteresis loop for three types of silica gel are examined in detail in order to illustrate the use and significance of DM values.

Regular density silica gel (fig. 4) has a hysteresis loop between 30-70% RH. If the designated RH range is 40-70%, the gel will be allowed to desorb down to 40% (Point A), at which point it is reconditioned. The sub-

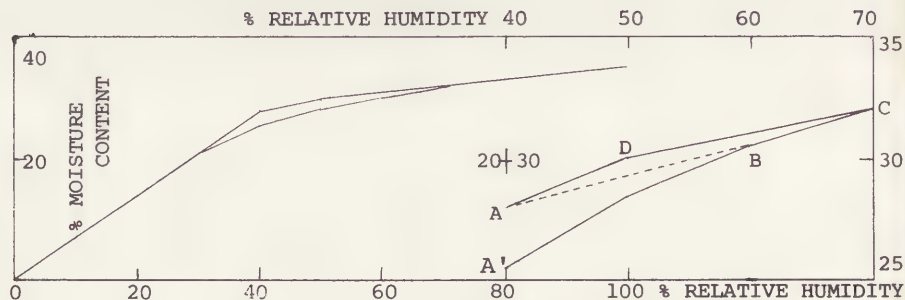


FIGURE 4 MC/RH Plot for Regular Density Silica Gel with Detail of Hysteresis Loop within the 40-70% Designated RH Range

sequent adsorption curve beginning at Point A will travel along path AB, intersecting the general adsorption curve at Point B. This area circumscribed by ABCD represents the designated hysteresis loop. Under these circumstances, the adsorption curve ABC and desorption curve ADC have average DM values of ± 1.3 (compared to general M values of $+2.3$ for A'BC and -1.3 for ADC).

Summary: Designated RH Range 40-70% RH

	40-70%	40-50%	50-60%	60-70%
M Value	$+2.3$	$+3.5$	$+2.0$	$+1.5$
	-1.3	-2.0	-1.0	-1.0
DM Value	$+1.3$	$+1.25$	$+1.25$	$+1.5$
	-1.3	-2.0	-1.0	-1.0

B type gel (fig. 5) has a very large hysteresis loop in the upper RH range, but it only begins at 50% RH. If, after reaching 70% on the adsorption curve (Point A), the gel desorbs moisture, it will generate a desorption curve which gradually slopes downward, reaching the general desorption curve at 60% RH (Point B). Any subsequent desorption will take place along the desorption curve (CB). Therefore, the functional hysteresis loop for B type gel between 40-70% RH can be described by loop ABCD.

Summary: Designated RH Range 40-70% RH

	40-70%	40-50%	50-60%	60-70%
M Value	$+4.3$	$+2.0$	$+3.0$	$+8.0$
	-11.0	-2.0	-6.0	-25.0
DM Value	$+4.3$	$+2.0$	$+3.0$	$+8.0$
	-4.3	-2.0	-6.0	-5.0

III type gel (fig. 6) is characterized by a large hysteresis loop between 30 and 80% RH. In order to derive the actual hysteresis loop for a 40-70% designated RH range, the following model is proposed. An adsorption curve lying within a hysteresis loop (BX, CY) is somewhat parallel to the initial adsorption curve (AW), except at the extreme limit where it finally combines with the initial adsorption curve; similarly, a desorption curve

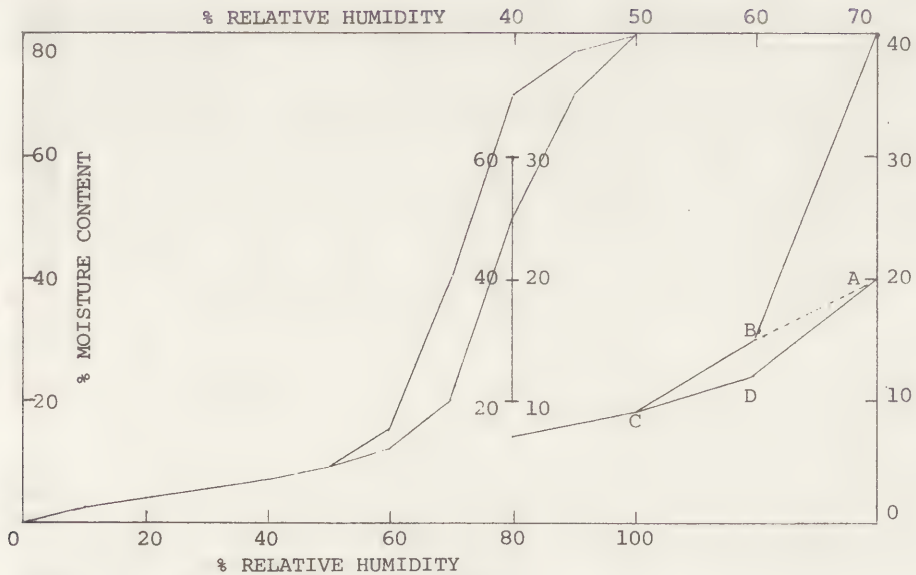


FIGURE 5 MC/RH Plot for B Type Gel with Detail of Hysteresis Loop within the 40-70% Designated RH Range

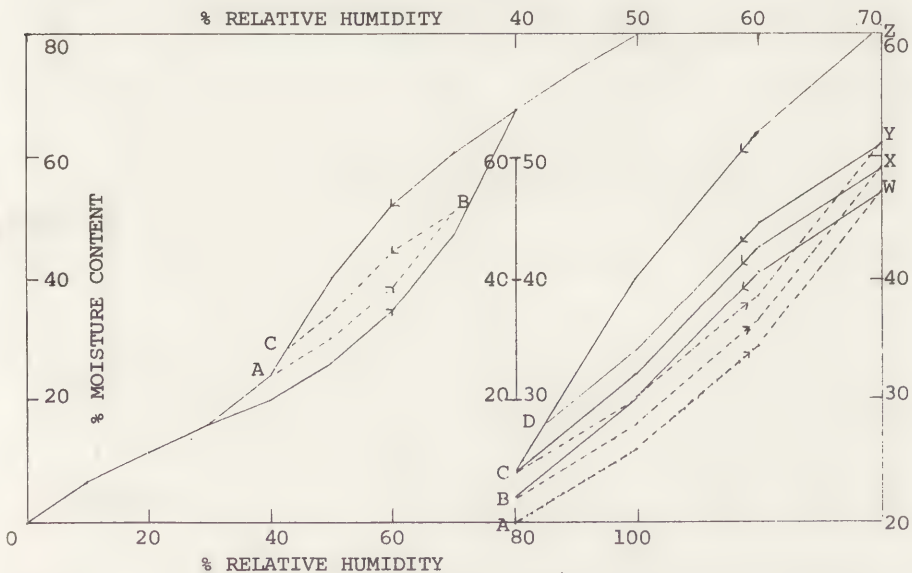


FIGURE 6 MC/RH Plot for Silica Gel III with Detail of Hysteresis Loop within the 40-70% Designated RH Range

within the hysteresis loop (WB, XC, YD) is similar to but flatter in character, especially near the terminal points, than the initial desorption curve (ZC). For the purpose of this approximate model, these adsorption-desorption curves within the hysteresis loop were drawn parallel to one another, and repeated until the adsorption curve finally branches from the initial desorption curve at or above 40% RH (CY). Open loops AWB and BXC are the non-repeatable, transitional loops which finally lead to loop CYD, representing the stable, repetitive designated hysteresis loop. Loop CYD also is represented in the 0-100% RH graph by ABC. As in the two previous examples, movement within this loop should produce average DM values similar to but slightly less than CY or YD.

	Designated RH Range 40-70% RH			
	40-70%	40-50%	50-60%	60-70%
M Value	+9.0 -12.2	+6.0 -16.0	+8.5 -12.0	+12.5 -8.5
DM Value	+9.0 -9.0	+6.0 -10.0	+8.5 -10.5	+12.5 -6.5

The DM values for different sorbents can be plotted, just as the M values were plotted in figure 2, in order to demonstrate the relative efficiency of a group of sorbents within a designated RH range. Figure 7 plots both the M- values and the DM- values for the three sorbents discussed above. The purpose for including the M values is to emphasize the importance of distinguishing between M and DM values when evaluating the efficiency of a sorbent.

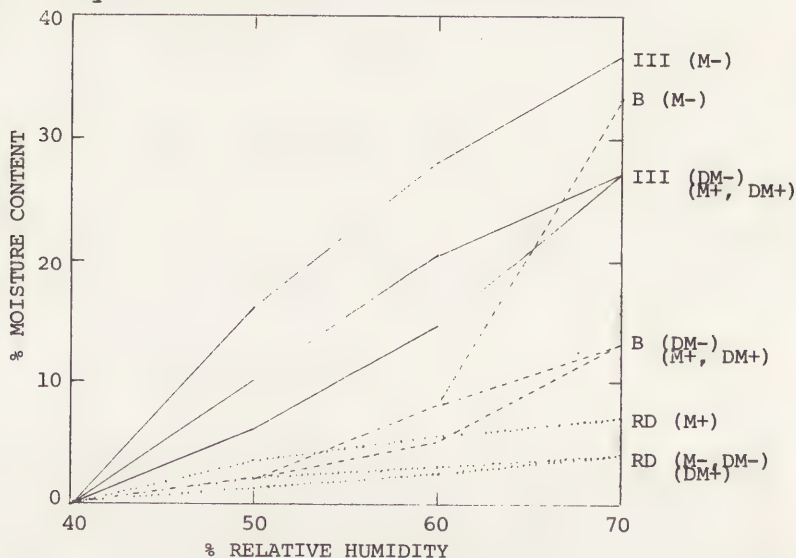


FIGURE 7 M^{\pm}/RH , DM^{\pm}/RH Plots for Three Sorbents within the 40-70% Designated RH Range

TEMPERATURE DEPENDENCE AND RESPONSE TIME

Two further characteristics of a sorbent that should be considered when determining the efficiency of a sorbent for a specific application is its temperature dependence and its response time. Response time depends upon the sorbent's inherent reaction time as well as such external factors as grain size and shape, and distribution within the showcase. These factors will be discussed by my colleague, Sadatoshi Miura, in the accompanying report.

CONCLUSION

There are a variety of silica gel and other sorbents available, some of which may be more appropriate for buffering changes in RH within an enclosed showcase than those presently in use. This paper has introduced a number of tools for determining which of these sorbents will be most efficient within a specific RH range.

Regular density silica gel is the most commonly used sorbent at present for humidity control within a showcase. Under 40% RH, the large decrease in its M value means that about five times as much gel must be used to equal the gel's moisture capacity at 20% or 30% RH. In many situations, it is not economically or physically feasible to use this quantity of sorbent for the higher RH range. The use of a more efficient gel in the higher RH range, one with a high DM value, makes it more practical to use sorbents in a high RH situation. Similarly, a sorbent which has a consistently high DM value throughout a designated RH range can greatly enhance the efficiency and practicality of a maintenance-free climate control showcase.

REFERENCES

- (1) Thomson, G., 'Stabilization of RH in Exhibition Cases: Hygrometric Half-time', Studies in Conservation, 22(1979), 88.
- (2) Weiser, H., Milligan, W., and Holmes, J., 'The Elimination of Sorption-Desorption Hysteresis in Hydrous Oxide Systems, Part I', J. Phys. Chem., 46(1942), 593-4.

81/18/5

STUDIES ON THE BEHAVIOR OF RH WITHIN AN
EXHIBITION CASE. PART II: THE STATIC AND
DYNAMIC CHARACTERISTICS OF SORBENTS TO
CONTROL THE RH OF A SHOWCASE

S. Miura

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting

STUDIES ON THE BEHAVIOR OF RH WITHIN AN EXHIBITION CASE.
PART II: THE STATIC AND DYNAMIC CHARACTERISTICS OF SORBENTS
TO CONTROL THE RH OF A SHOWCASE

S. Miura

Tokyo National Research Institute of Cultural Properties
13-27, Ueno-Park
Taito-ku
Tokyo 110
Japan

ABSTRACT

The 'static' and 'dynamic' characteristics of a buffer were examined in order to estimate the ability of a sorbent to buffer changes in RH within a showcase. The moisture content, hysteresis and response time of three sorbents, a regular density silica gel, an intermediate density silica gel, and Nikkapellet were examined. The delaying effect of hysteresis on response time was demonstrated. The importance of a sorbent's physical characteristics and temperature dependence were discussed. Methods for improving response time by using a fan to aid circulation, improving the distribution of the sorbent, and by the use of silica gel powder were tested.

1. INTRODUCTION

In the 1978 ICOM Conference on Climatology in Museums, there was a general consensus that a non-mechanical relative humidity (RH) control system will be used more and more because of its convenience and low cost. To control RH within such a showcase, two types of buffering material, or sorbent, frequently used, regular density silica gel (in many countries) and Nikkapellet (in Japan). The choice of a suitable sorbent is based on its moisture content/relative humidity (MC/RH) curve. But the actual ability to stabilize RH within a showcase involves other factors as well. The hysteresis and temperature dependence of the sorbent are also important. Together, these three factors represent the 'static characteristics' of the sorbent. Other factors, such as inherent response time, size, shape and distribution of the sorbent, referred to as 'dynamic characteristics' are also very important in stabilizing RH within a showcase.

This paper will present some preliminary tests intended to estimate the actual ability of a sorbent to control RH. The experimental results will be used to explain the

relationship between hysteresis and response time, and the general significance of both the static and dynamic characteristics of a sorbent on its ability to control the RH of a showcase will be discussed.

2. EXPERIMENTAL SET-UP

2.1 TYPES OF SORBENT TESTED

Three types of sorbent were examined in this report: 1) Nikkapellet, used in Japan in preference to regular silica gel because of its larger moisture capacity under conditions of high RH, 2) A type silica gel, a regular density silica gel, similar to regular density (RD) gel produced by W.R. Grace and Co. in the U.S.A. and 3) B type silica gel, an intermediate density silica gel.

2.2 STATIC CHARACTERISTICS

For each type of silica gel, the MC/RH curve at a specific set of RH values was derived from the author's own tests applying Japanese Industrial Standards (JIS) procedures.

Sorbents were put in dessicators of a constant RH, generated by saturated salt solutions of MgCl_2 (33%), K_2CO_3 (43%), $\text{Mg}(\text{NO}_3)_2$ (54%), NaCl (75%) and KNO_3 (95%), all at 20°C, for 48 hours. Then they were measured after drying for two hours at 160-170°C.

As was discussed in the previous paper, the MC/RH curves included here should be considered approximate because of variations in different batches of the same type of silica gel. In particular, B type silica gel has a large variation in the starting point of its large increase in adsorption capacity and in its accompanying hysteresis curve.

2.3 DYNAMIC BEHAVIOR

A showcase was made of transparent acrylic sheet (8 mm), and was placed in a chamber which can be controlled to any temperature and RH. The dimensions of the case are 1.5 m wide, 0.6 m deep and 1.5 m high (about 1.4 m³ in volume). After a sorbent was set at the bottom of the showcase, the temperature of the chamber was raised from 20°C to 30°C. Changes in the temperature and the humidity within the showcase were continuously measured at its lower and upper part by thermocouples and electro-hygrometers and the vapor pressure was derived from this data.

3. RESULTS AND DISCUSSION

3.1 STATIC CHARACTERISTICS

Figure 1 shows MC/RH curves of three types of sorbent,

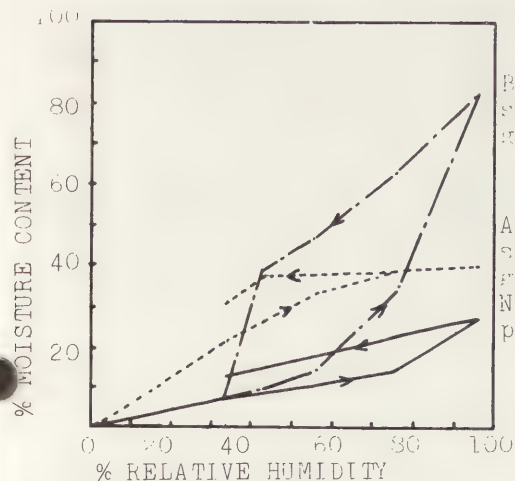


Fig.3 Moisture content/relative humidity curve

This moisture capacity represents the sorbent's M value, discussed by my colleague, Steven Weintraub, in the previous paper. Here, the mean M values would be 4 and 8 respectively.

However, it is very important to notice the difference in gradient between the adsorption curve and the desorption curve. In fact, A type silica gel has a greater gradient than Nikkapellet on the adsorption curve, but, to the contrary, its gradient is very small at the desorption curve. In order to note this considerable difference, the gradient of the adsorption curve is given an M+ value and the desorption curve an M- value. Then we can easily know the difference and the ability of a sorbent to buffer changes in RH. These difference in M value are given in Table 1. This shows that while A type gel has an M+ value between that of B type and Nikkapellet, it has an M- value one fourth that of Nikkapellet and one sixteenth that of B type gel.

Table 1 M+ and M- values
between 50-70% RH
M+ value M- value

A type silica gel	+4	-0.5
B type silica gel	+8	-8
Nikkapellet	+2	-2

This means that on the desorption curve, the sorbent must release moisture into the drier air (it may occur in many museums in winter). In this case, A type silica gel is not so effective, and a large quantity of A type silica gel must be used for stabilizing the RH within a showcase.

Since, in the experiments discussed below, RH within

A type and B type silica gel, and Nikkapellet. From these curves, the moisture capacity for a given change in RH can be determined. For example, 100g of A type silica gel adsorbed about 8g H₂O against a change in ambient RH from 50 to 70%, while the same quantity of B type silica gel adsorbed about 16g H₂O. From this, we know the capacity of B type silica gel is twice that of A type silica gel in the range of 50-70% RH.

a showcase changed from high to low when the ambient temperature was raised from 20°C to 30°C , the desorption MC/RH curve (i.e. M- value) was most important.

3.2 DYNAMIC CHARACTERISTICS

To estimate the ability of a sorbent to stabilize RH in a showcase, it is essential to know how long it takes for a sorbent to bring the RH within a showcase back up to its initial RH. If the RH returns very slowly, art objects within the showcase may suffer a change in moisture content due to the ambient RH change, and, in severe cases, a distortion or a crack will probably occur. For this reason, a buffering material which responds very slowly can not be used for buffering changes in RH, whatever M value it has.

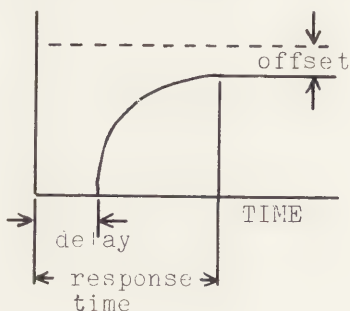


Fig.2 Typical and simple response curve

In order to estimate the actual response of a sorbent to changes in RH under dynamic conditions, a response curve is used. Figure 2 is a typical and simple response curve showing an offset (permanent deviation from a set point), a response time (time for almost arriving at a final value) and a delay (time until the beginning of the response).

Since the M value corresponds to the capacity of a sorbent to buffer changes in RH, it affects the offset. If a sorbent has a small M- value and its quantity within a showcase is not enough, RH will not be able to reach a desired level when the temperature changes, and a considerable offset will remain.

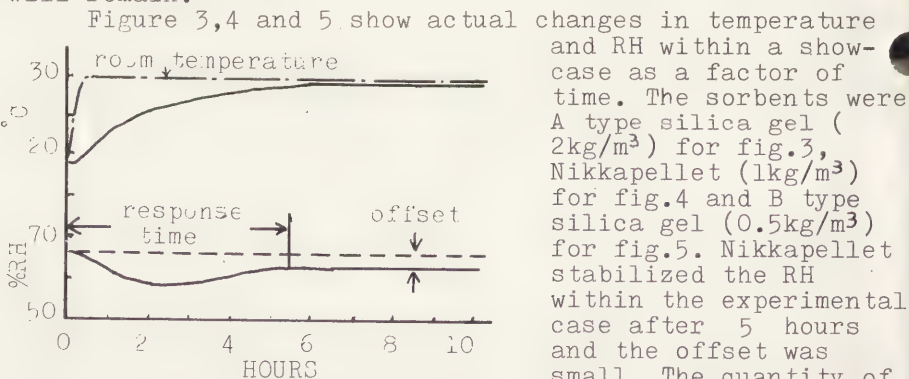


Fig.3 Changes in temperature and RH within a showcase (A type silica gel 2kg/m^3)

and RH within a showcase as a factor of time. The sorbents were A type silica gel (2kg/m^3) for fig.3, Nikkapellet (1kg/m^3) for fig.4 and B type silica gel (0.5kg/m^3) for fig.5. Nikkapellet stabilized the RH within the experimental case after 5 hours and the offset was small. The quantity of B type silica gel is only half, but its offset was still small

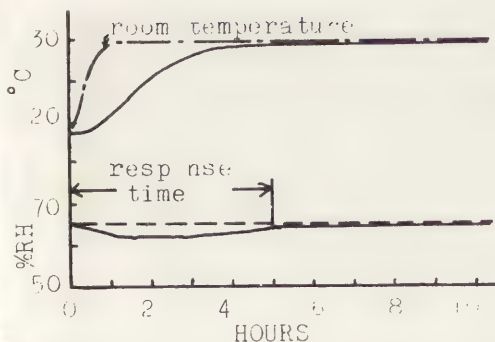


Fig. 4 Changes in temperature and RH within a showcase (Nikkapellet 1kg/m^3)

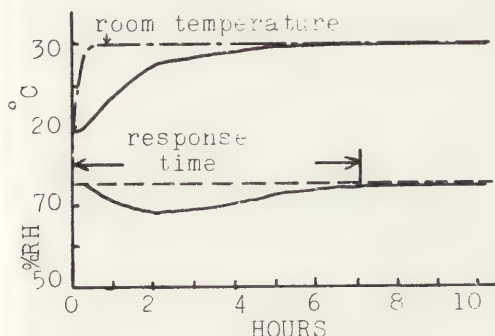


Fig. 5 Changes in temperature and RH within a showcase (B type silica gel 0.5kg/m^3)

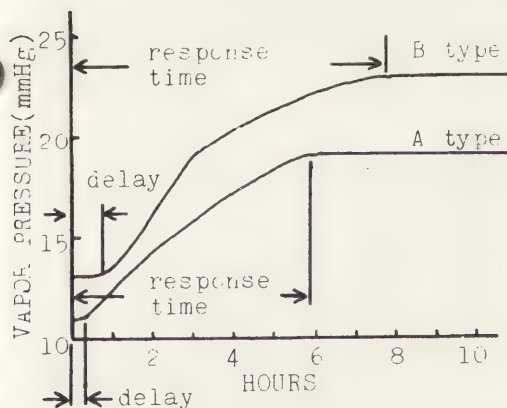


Fig. 6 Vapor pressure changes within a showcase

because of its large M -value. However, in the case of A type silica gel, an offset of about 4% RH remained in spite of the fact that twice as much sorbent was used as Nikkapellet and four times as much as B type gel.

When a material has a large hysteresis, discussed in the previous paper, the actual or DM-value within the hysteresis loop will be somewhat smaller than its theoretical value. Furthermore, the response of a sorbent is likely to show a significant delay at the beginning of its response curve due to hysteresis.

Figure 6 shows vapor pressure changes within a showcase containing A type and B type silica gel as the sorbent. When silica gel releases moisture according to its desorption curve, the vapor pressure within the showcase will increase; thus, the vapor pressure change indicates a buffering effect. By comparing the beginning of a response curve measuring vapor pressure, the delay of B type silica gel is slightly larger than A type silica gel, probably because of its large hysteresis. But due to its large M -value, B type silica gel soon

surpassed A type silica gel.

Thus, hysteresis (an inherent factor) caused a delay in the response of a sorbent. Physical and external factors may also be important to the speed of response, such as: size and shape of the sorbent particles, the exposed surface area and depth of the sorbent and its arrangement within the showcase.

These non-inherent factors are actually more important in terms of allowing the entire quantity of sorbent to effectively respond to changes in RH.

(1) Shape

A grain of crushed silica gel has a larger surface area for its volume than the bead type and is individually more responsive. In depth, the bead type has a larger void area surrounding each bead and offers less resistance to the passage of air through the depth of the gel. In a showcase where air velocity is minimal (less than 0.1m/s), the bead variety is probably superior if it is packed more than a few grains deep.

(2) Size

The smaller the grain particle, the more quickly will the entire grain come into equilibrium with a new RH. However, in depth, the smaller type of gel will have smaller void spaces surrounding each grain and will provide greater resistance to air flow into the lower layers of gel. As in the case of shape, if a thick layer of gel is used, it is preferable to use a larger grain size in order to improve air circulation within the gel depth.

(3) Surface Area

The larger the interface between air and gel, the quicker the response. Therefore, as much gel as possible should be exposed to the surface for good response time.

(4) Depth

The greater the depth of gel, the less responsive it will be in the lower layers.

(5) Arrangement

In order to insure uniform response throughout the showcase, the gel should be distributed as evenly and extensively as possible throughout the case.

This is most essential and will be discussed further in the following section.

(6) Temperature Dependence

Since the MC/RH curves of many moisture sensitive materials are affected by temperature, the M value and response time will vary with a change in temperature. Therefore, to maintain the consistent M value necessary to stabilize RH within the case, the sorbent's MC/RH curve should be independent of temperature effects in the anticipated temperature range.

3.3 IMPROVEMENT OF RESPONSE TIME

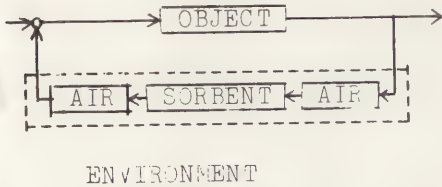


Fig.7 Flow-chart of moisture within a showcase

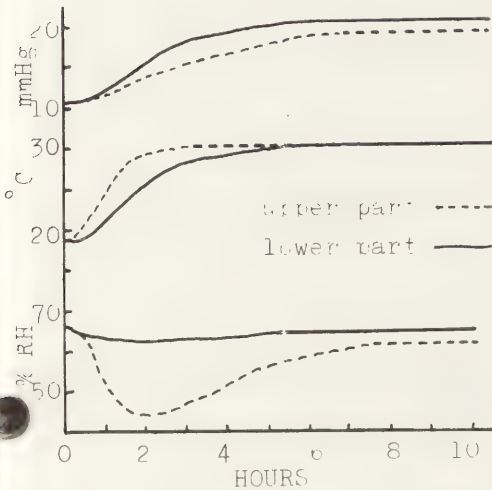


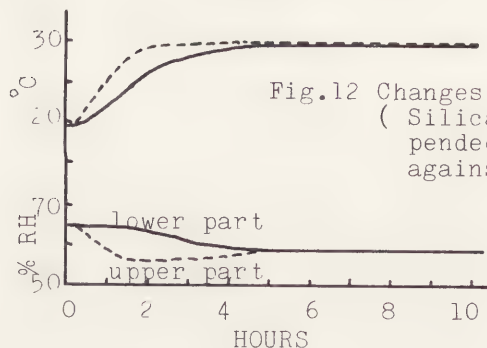
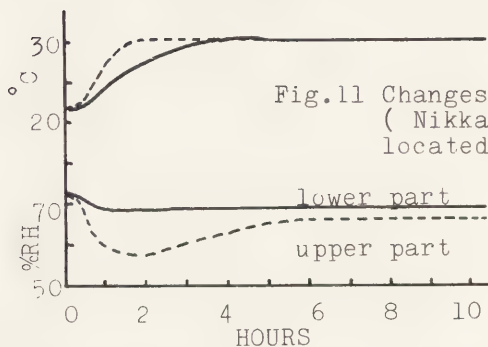
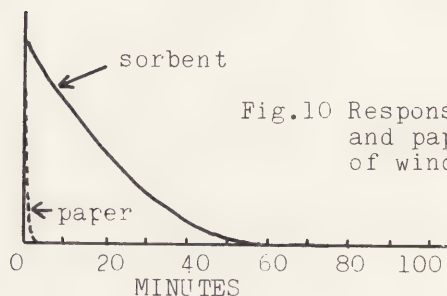
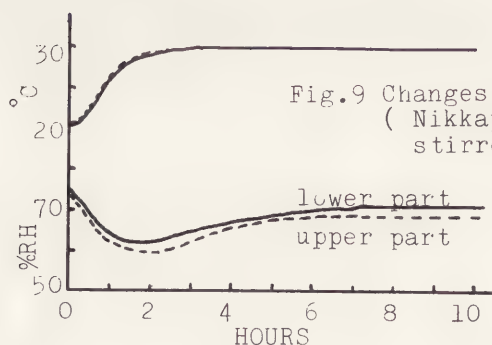
Fig.8 Changes within a showcase (Nikkapellet 1kg/m³)

speed of about 0.5m/s). Figure 9 shows that the diffusion rate of RH was almost the same for both the bottom and top of the case.

However, an air flow is injurious to many art objects such as 'Urushi' (Japanese lacquer) and works of art on paper. When air flows around paper, its response will be quick. On the other hand, the response of the sorbent is slower in spite of the existence of wind (figure 10), so the buffer can not follow a change in the moisture of the paper, that is, it will be ineffective in preventing a

Figure 7 shows a flow-chart of moisture within a showcase. The air acts as the transfer medium for moisture between the object and sorbent. The response time within a case must also take this transfer rate into account. An experiment was designed to test transfer speed where temperature, RH and vapor pressure were measured in the lower part of the experimental showcase, in close proximity to the sorbent, and in the upper part of the case, at a maximum distance from the sorbent. Figure 8 shows the results of such a test using Nikkapellet as the sorbent. While the RH and vapor pressure rose rapidly in the lower part of the case, the response rate was considerably slower in the upper part, due to the slow diffusion of moisture through the air.

In order to improve the rate of diffusion, the air within the showcase was stirred by a fan (wind



change in the moisture content of the paper. Thus, it may not be advisable to stir the air within the showcase.

The difference in response time between the lower and upper parts of the case also can be reduced non-mechanically by improving the distribution of sorbent within the case. Figure 11 shows a response curve where the Nikkapellet is located along the wall of the case. Although this represents an improvement over figure 8, where the sorbent was located at the bottom of the case, there is still a considerable general delay in response due to the slow response time of the sorbent itself.

A much more rapid response is possible by using a sorbent in its powdered form. Because of its very large surface/air interface, powdered silica gel will respond very quickly to a change in RH. Specially prepared paper and plastic sheet impregnated with fine silica gel powder can be used for this purpose. Figure 12 represents a case containing such silica gel sheets suspended vertically against the wall of the case. The change in RH in both the upper and lower parts of the case were small and the case stabilized quickly after about five hours.

4. CONCLUSION

The observations and recommendations made in this paper can be used as check-points in using a sorbent most efficiently in an actual showcase situation. These points are summarized below:

- (1) Moisture Capacity --- The moisture capacity of a sorbent must take hysteresis into account. The use of M+ and M- values, or, more accurately, DM+ and DM- values, will indicate the sorbent's true ability as a buffer. A large DM⁺ value will result in a small offset in RH.
- (2) Hysteresis --- Since hysteresis will cause a delay in the sorbent's response time, this should be considered when estimating the initial response time of a sorbent.
- (3) Physical Factors --- Shape, size, surface area and depth should be carefully chosen to maximize the gel's ability to respond.
- (4) Temperature Dependence --- The sorbent should be temperature independent in the anticipated temperature range to be sure of consistent results.
- (5) Arrangement --- The sorbent should be distributed as uniformly as possible throughout the case to insure a uniform RH within the case.
- (6) Speed of Response --- Since all sorbents in granular form require a significant period of time to respond to sudden RH changes, a more rapid response can be achieved

with the sorbent in its powdered form, i.e. impregnated paper or plastic sheet.

It is hoped that the results of these two reports will be used as a basis for developing a safe, efficient and inexpensive environment that can be used for the preservation as well as the display of works of art throughout the world.

REFERENCES

1. Toishi, K., 'Humidity Control in a Closed Package', Studies in Conservation, 4(1959), 81-87.
2. Thomson, G., 'Stabilization of RH in Exhibition Cases: Hygrometric Half-time', Studies in Conservation, 22(1979), 85-102.

81/18/6

STABILISING RELATIVE HUMIDITY VARIATION
WITHIN DISPLAY CASES: THE ROLE OF SILICA
GEL AND CASE DESIGN

B.L.Ramer

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting

STABILISING RELATIVE HUMIDITY VARIATION WITHIN DISPLAY
CASES: THE ROLE OF SILICA GEL AND CASE DESIGN

B.L.Ramer

Sainsbury Centre for Visual Arts
University of East Anglia
Norwich, Norfolk NR4 7TJ
Great Britain

ABSTRACT

The aspects of a system of local humidity control for museum display cases are discussed, in which a description of the methods employed to condition and install silica gel at the Sainsbury Centre for Visual Arts is given. The monitoring process is also outlined, the results of which are illustrated to indicate the stabilising effect of the humidity buffer.

In an experimental section, it is shown that diffusion is the chief mechanism for air exchange between the interior of a display case and its surroundings. In turn, the results of the experiment are used to calculate the number of air changes per day which occur.

1. INTRODUCTION

In 1973 Sir Robert and Lady Sainsbury gave their personal collection of antiquities, ethnographic objects and works of art to the University of East Anglia, as well as an endowment primarily designed to enable the University to construct a building to house the collection. Completed in 1978, the Sainsbury Centre for Visual Arts is essentially a long, open-ended structure in which both the east and west ends consist of large panels of glass joined by a clear adhesive. Enclosing the walls and roof is the supporting structural system of welded steel tube together with a cladding system of interchangeable aluminium and glass panels.

Reflecting the Sainsbury's belief that students of Art History should equally learn the pleasures of visual experience, the main exhibition gallery, the Living Area, is furnished with carpeting and comfortable chairs. Natural top lighting, controlled automatically by internal motorised louvres, provides a large proportion of the exhibition lighting. Furthermore, in keeping with the spirit of a living room environment, the building is not equipped with an air-conditioning system. In the context of a lightweight contemporary structure lacking such a form of environmental control, this paper describes the non-mechanical system of local humidity control developed for the display cases in the Sainsbury Centre.

2. CONDITIONING

Normally the dry silica gel is conditioned to either of two levels: 55% RH for objects created from organic material such as wood, ivory and leather, or approximately 40% RH for metal artifacts. In addition, when these two types of humidity-sensitive material have been exhibited within the same display case, it has been necessary to condition the silica gel to a point anywhere between these two RH levels. In these situations the most vulnerable object in the case will usually dictate the appropriate Relative Humidity required.

Initially, the silica gel was conditioned within a standard laboratory humidity cabinet using saturated solutions of various salts. To allow for adequate air circulation the glass shelves supplied with the cabinet were replaced with porous trays. More recently, however, an environmental chamber available at the University enables the conditioning process to be run more efficiently. Here, known quantities of silica gel are thinly spread over a number of buffet trays stacked within the chamber. The method employed to determine the Equilibrium Moisture Content of the silica gel from small samples of known weight is parallel to that outlined by Stolow [1.].

Having completed the conditioning process, the silica gel is stored inside muslin bags to allow for adequate air circulation once the bags are placed inside the display cases. A Velcro strip sewn along one edge of each bag eases handling and regeneration of the gel when necessary. The amount of silica gel placed inside each bag, as well as the size of the bag itself, are related to the modular design of the display cases. Each bag, labelled with information relevant to the conditioning process, is then sealed inside a polythene bag before being stored inside a polypropylene container. If the conditioned silica gel is to be stored for long periods of time, air-tight containers are also employed.

3. INSTALLATION OF SILICA GEL

The materials chosen to construct our free-standing display cases, their size and the stringent specifications which accompanied their design have enhanced the provision of stable micro-environments. The metal plinths are made from mild steel with a stove enamel finish; the tops, fabricated from high quality perspex (8 mm thick), possess mitred joints which are chemically welded. Diffusion between the interior of the case and the surroundings is therefore minimised. In addition, the wooden board supporting the objects, and the display fabric covering it, act as humidity buffering agents alongside the silica gel. Furthermore, the conditioning process of the silica gel as well as its installation requirements have been simplified since the majority of the free-standing display cases have been built to a standard size, thereby facilitating the adoption of a modular approach to local humidity control.

For a museum which employs an open plan scheme in its exhibition areas and, equally, which lacks air-conditioning, this straightforward, flexible approach to local environmental control has proved to be invaluable. Thus, as part of this open plan system, display units are rearranged to establish new relationships between works of art of different cultures; and it has been possible to re-establish humidity control for these objects placed in another part of the gallery.

In as much as the display cases are well-built units, their initial design did not incorporate a system of local humidity control since they were manufactured prior to the appointment of a conservator to the Sainsbury Centre. Nevertheless, by exploiting the existing features of the initial design, it has been possible to adapt these cases to accommodate silica gel. Figure 1, a cross-section of a standard-size display case, illustrates the result of these refinements.

In order to store the silica gel within the case, it was decided to design a lightweight, durable tray which could fit snugly inside the metal plinth. Each tray, cast in stabilised polyvinyl chloride, possesses a rim designed to rest on the interior metal lip located at the top of the plinth. Siting the tray here brings the silica gel, having been spread evenly across the floor of the tray, as close as possible to the objects above. To reduce the volume of air in need of humidity control, and thereby reduce the quantity of silica gel required, the rim of the tray is securely taped to this interior lip of the plinth. This has also served to localise the volume of space of most concern in a situation where it has not been possible to incorporate an access door in this second phase of the display case design.

Placing a draught excluder along the inside edge of the metal lip where the perspex top is positioned on the plinth minimises diffusion between the interior of the case and its surroundings. Holes are drilled into the display board prior to covering it with fabric to facilitate air circulation between the silica gel and the display space above. Lastly, holes drilled into a number of components of the display case unite these components for the purposes of security: a specially designed screw is passed through the plinth, perspex top and display board into the metal protrusion situated at the four corners of the interior lip of the plinth. The above-mentioned adaptations to the initial design of these display cases represent a move towards protecting each object from the surrounding environmental conditions; thus, in the efforts to achieve a reasonably air-tight case, it has been equally important to test the stability of the various display components by the methods outlined by Blackshaw and Daniels [2.].

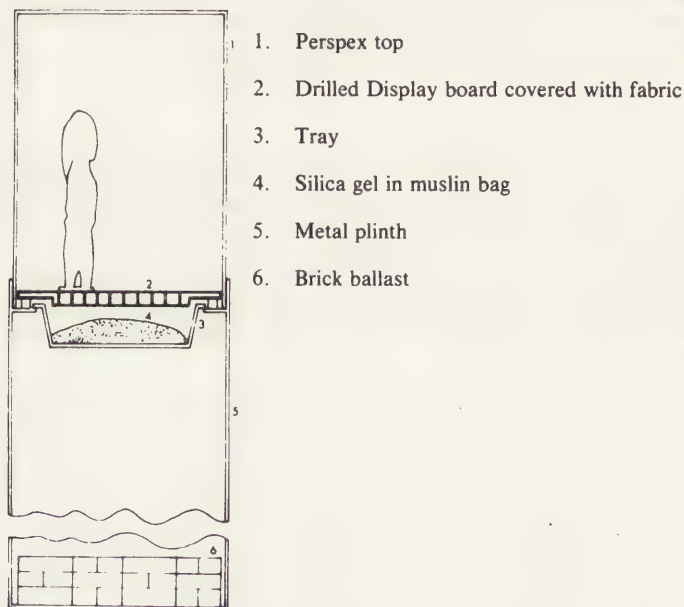


FIGURE 1. CROSS-SECTION OF A STANDARD-SIZE DISPLAY CASE, 1800 mm x 600 mm x 600 mm, ADAPTED TO ACCOMMODATE SILICA GEL.

4. MONITORING

Various quantities of conditioned silica gel were placed in these standard-size cases when the Sainsbury Centre opened in order to estimate the amount of buffer necessary to stabilise seasonal RH variation for a reasonable period of time. In particular, this project was designed to test Thomson's recommendation of 20 kg of silica gel per cubic metre of case volume [3.].

The conditions within each display case were measured with a thermohygrometer while a thermohygrograph installed in the gallery recorded the ambient conditions on a day-to-day basis for each week. A standardised form, the Weekly Temperature and Relative Humidity Report, was used to document the thermohygrometers' readings. These readings were noted down in the early morning and mid-afternoon throughout the week.

With the assistance of the University's Computing Centre and School of Environmental Sciences, it has been possible to employ the two forms of weekly records for an assessment of the environmental behaviour of the Sainsbury Centre and its display units. A number of Fortran IV programs use these records as input data and convert the information into graphical form and line printer listings.

With respect to the weekly charts of the thermohygrograph, a digitizer table or tablet converts the RH and temperature recordings into a machine readable form on paper tape. Once verified, this data is input to a program which lists the week's RH and temperature recordings at the two hour intervals printed on the chart of the thermohygrograph. A sub-routine within the program scales the data to correct for the curvature of the lines which are printed on the chart as well as the time displacement of the two indicator pens. Additional programs are then used to calculate the daily and monthly averages of RH and temperature from the two hour values.

By means of a Fortran graphical package these daily averages for the year are output in graphical form. The daily RH readings within a display case are also averaged and then output on the same graph to correlate the Relative Humidity inside the case with the ambient conditions of the gallery (Figure 2).

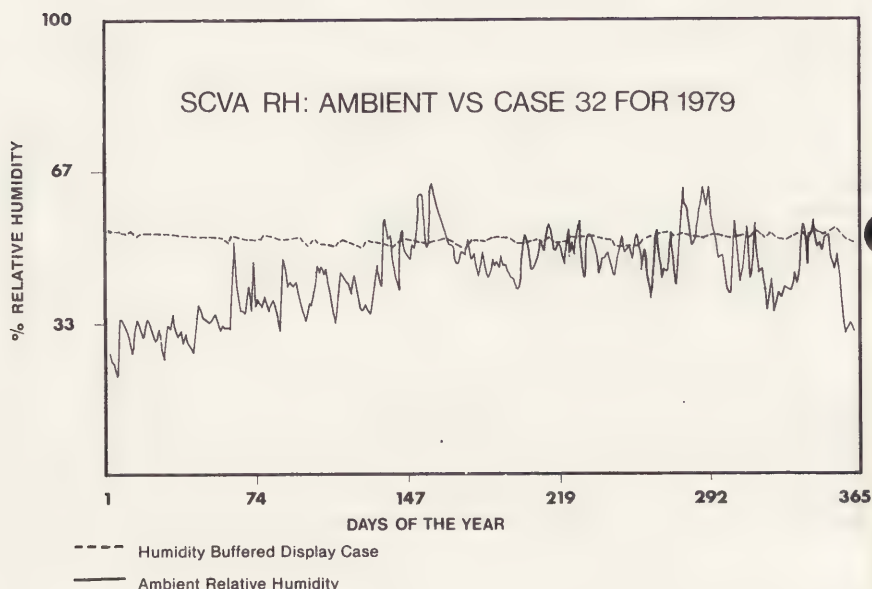


FIGURE 2. THE RH VARIATIONS OF THE MAIN EXHIBITION AREA AND CASE 32 FOR THE YEAR 1979.

Towards the end of 1978, case 32 (a standard-size case containing a standing female figure in wood from the Ivory Coast), was filled with silica gel conditioned to 55% RH. The amount installed was proportional to the recommendation of 20 kg of silica gel per cubic metre of case volume. In order to bring the object and the display components as close as possible to the RH level of 55%, the standing female figure and the silica gel were installed in the case in the late autumn, a period when the ambient Relative Humidity approaches an average of 55%.

5. EXPERIMENTAL

5.1 Mechanism of Air Exchange in a Display Case.

In order to study the mechanism of air exchange between the interior of a display case and its surroundings, an experiment was designed using a tracer gas method to monitor the concentration of various gases within a standard-size display case over a period of time. Only non-reactive gases could be introduced into the display case to avoid any damage to the object. Initial trials were made with freons, but these have not yielded suitable results so far.

Using the gases naturally present in the display case provided an alternative approach to the experiment. A large volume of nitrogen was passed into the case via the screw hole where the perspex top is secured to the metal plinth. Increasing the concentration of nitrogen acted to deplete the oxygen level to approximately one half its normal value. Immediately after the introduction of nitrogen, a small volume of carbon dioxide was added, which increased the carbon dioxide level of the air in the case to about ten times its normal value. A rubber septum was then used to seal the screw hole.

In the days that followed small samples of gas were extracted through the septum with a syringe. Each sample was then injected into a gas-liquid chromatograph so that the oxygen and carbon dioxide content could be determined. In this way the gradual loss of carbon dioxide and invasion of oxygen was monitored.

The results can be seen in Figure 3, which is plotted on a semi-logarithmic scale so that any anticipated changes of an exponential nature would appear linear. The half-lives for the exchange of the gases with the display case were then calculated to be:

Oxygen	2.3 days
Carbon dioxide	2.7 days

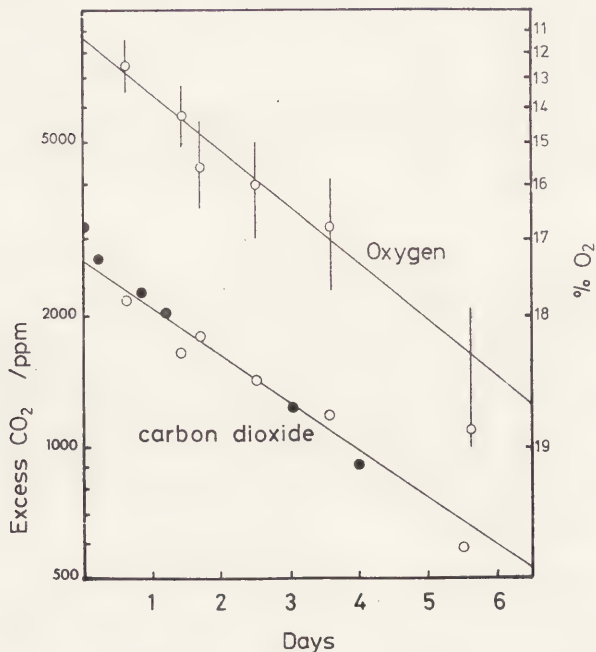


FIGURE 3. CHANGE IN CONCENTRATION OF CARBON DIOXIDE AND OXYGEN WITH TIME FOR EXPERIMENTAL DISPLAY CASE.

Carbon dioxide, being heavier than oxygen, diffuses more slowly and is thus consistent in qualitative terms with Padfield's work which indicates that the air exchange process occurs essentially by diffusion [4.]. Equally, the results confirm Thomson's studies which show that the exchange of air within a display case, and hence water vapour variation, occurs exponentially [3.].

From Graham's Law of diffusion, recognising that the temperatures and pressures of the gases within the case and the surrounding environment are the same, and thus have the same molar volume,

$$k_1 / k_2 = (MW_2 / MW_1)^{\frac{1}{2}} \quad \dots (i)$$

where k_1 and k_2 are the diffusion rate constants and MW_1 and MW_2 are the molecular weights of the gases. Furthermore, the following relationship relates diffusion rate to half-time,

$$t_{\frac{1}{2}} = -\frac{1}{k} \log_e \frac{1}{2} = 0.693/k \quad \dots (ii)$$

(see, for example, Thomson [3.]).

Hence combining equation (i) and (ii) for the two gases we get after some re-arrangement,

$$(t_{\frac{1}{2}})_1 / (t_{\frac{1}{2}})_2 = (MW_1 / MW_2)^{\frac{1}{2}} \quad \dots (iii)$$

The difference in the half-life of carbon dioxide when compared to oxygen is therefore related to their molecular weights, and the half-life of the former gas can be estimated from the oxygen data in Figure 3:

$$t_{\frac{1}{2}}(CO_2) = 2.3 / (32/44)^{\frac{1}{2}} = 2.7 \text{ days}$$

which is precisely the measured value for carbon dioxide. This therefore confirms Padfield's estimation that the air exchange process within a display case is essentially by diffusion. Water, with a molecular weight of 18, is lighter than both carbon dioxide and oxygen; and its half-life can be estimated from either of the results to be 1.73 days.

5.2 Calculation of Air Change Rate

From Figure 3, we note that the concentration of carbon dioxide is 2000 ppm after 1.24 days, and 1000 ppm after 3.94 days. The concentration of carbon dioxide in the exhibition areas varies slightly but is typically 400 ppm. The air change rate A is related to the concentration C_1 at a time t_1 by [5.],

$$\left(\frac{C_1 - C_s}{C_0 - C_s} \right) = e^{-At_1}$$

where C_0 is the initial concentration, and C concentration of carbon dioxide in the exhibit. Thus if we measure the concentration at two times t_1 and t_2 , we can estimate the air change rate

the area. in time, if we

do not know the initial concentration, as we can obtain the following:

$$A = \frac{1}{(t_1 - t_2)} \log_e \left(\frac{C_2 - C_s}{C_1 - C_s} \right)$$

where C_2 is the concentration at time t_2 . Substituting the above values gives:

$$A = 0.363 \text{ changes per day implying} \\ \text{one air change in 2.75 days.}$$

This estimate using carbon dioxide as the tracer gas will give an over-estimate of time required for one air change. Noting that the molecular weight of air is approximately 29, we can estimate the time air change rate as,

$$0.363 \times \left(\frac{44}{29} \right)^{\frac{1}{2}} = 0.448 \text{ air changes per day} \\ \text{or one air change in 2.23 days.}$$

5.3 Hygrometric Half-Time

By monitoring the RH change in our standard-size display cases equipped with various amounts of silica gel, it was hoped that a low maintenance system for humid buffering could be derived from the hygrometric half-time calculated for each case. Case 32, filled with silica gel in the proportion of 20 kg per cubic metre of case volume, was of particular interest throughout this monitoring period. Assuming a change of approximate 10% RH is necessary to determine the hygrometric half-time of a case properly [3.], it was felt a calculation of such a half-time for this case would be inexpedient since a sufficient RH drift had not occurred. Furthermore, the theoretical approach of Thomson is only applicable if the Relative Humidity of the galleries do not vary to a large extent. In our exhibition areas the daily variation is often significant: typically 10-20% in summer, as is the seasonal variation, fluctuating from 30% in winter to 70% in summer. A more general analysis is thus needed to assess the hygrometric half-time.

Figure 2 compares the ambient RH variation within the main exhibition area with that within case 32. In 1979, the RH readings of the case decreased from about 54% to 51% over the year. It is clear that this amount of silica gel can satisfactorily buffer RH variations for periods of twelve to eighteen months before replacement.

needed to be considered. Case 94, on the other hand, another standard-size display case proportionately filled with half the recommended amount (20kg) of silica gel did not provide the same level of stability. The RH readings in this case decreased from about 53% to 46% over the same period.

6. CONCLUSIONS

Silica gel provides an effective means of buffering RH variation within display cases. Anyone calculating the amount of silica gel to install in a display case is advised to follow, at least initially, the recommendation of 20kg per cubic metre of case volume. As it has been shown that diffusion of air is the important cause of RH variation within display cases, good case construction is essential. Reducing leaks to the surroundings extends the hygrometric half-time value. Standardisation of display case volume whenever possible facilitates the conditioning of the humidity buffering agent as well as its installation within cases. Equally, a systematic approach to environmental monitoring will assist the assessment of the behaviour of the buffering agent.

MATERIALS

Regular density silica gel, particle size 2.5 - 6 mm, is purchased from W. R. Grace Ltd., Northdale House, North Circular Road, London.

Velcro is the trade name for a flexible, pressure-sensitive hook and lock fastener commonly used in the manufacture of sportswear and upholstery.

REFERENCES

1. Stolow, N., 'The Effectiveness of Preconditioned Silica Gel and Related Sorbents for Controlling Humidity Environments for Museum Collections.' Paper given at ICCROM Conference on Climatology, Rome, 7-10 November 1978.
2. Blackshaw, S., and Daniels, V., 'Selecting Safe Materials for Use in the Display and Storage of Antiquities.' ICOM Committee for Conservation, 5th Triennial Meeting, Zagreb, 1978.

3. Thomson, G., 'Stabilization of RH in exhibition cases: Hygrometric Half-Time', Studies in Conservation 22(1977), 85-102.
4. Padfield, T., 'The Control of Relative Humidity and Air Pollution in Show-cases and Picture Frames', Studies in Conservation, 11(1966), 8-30.
5. Bassett, C., and Pritchard, M., Environmental Physics: Heating, Longman, London, 1969.

ACKNOWLEDGEMENTS

I wish to thank the following individuals at the University of East Anglia for their advice and assistance: Dr. P. Brimblecombe, Dr. K. Tovey, Mr. T. Winnington, all of the School of Environmental Sciences, and Mr. R. Johnson, Graphic Design.

POURQUOI LES CONSERVATEURS N'UTILISENT-ILS
PAS LE GEL DE SILICA OU LES TROIS USAGES
DU GEL DE SILICE

Gaël de Guichen

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Contrôle du climat et
de l'éclairage

POURQUOI LES CONSERVATEURS N'UTILISENT-ILS PAS LE GEL DE SILICE OU LES TROIS USAGES DU GEL DE SILICE

Gaël de Guichen

ICCROM
13 via di san Michele
00153 Rome
Italie

Resumé

Les matériaux-tampon, et principalement le gel de silice, offrent de très belles perspectives pour contrôler le climat d'une manière très sûre et peu onéreuse dans les vitrines de musée. Par méconnaissances, les conservateurs ne l'utilisent pas, peu ou mal. L'article cherche à donner une information de base sur le gel de silice afin de permettre à un non scientifique de lire les articles plus spécialisés.

Introduction

Le gel de silice est largement utilisé dans les musées car il a la réputation d'être un produit miracle. Beaucoup de conservateurs ont en effet l'espoir de pouvoir se décharger sur le gel de silice de leur responsabilité de l'environnement des collections et en particulier de contrôler l'humidité relative.

Ravivée par certains articles flatteurs et propagée de bouche à oreille, la bonne renommée du gel de silice est telle qu'un aucun conservateur de musée ou restaurateur ne se permettrait de mettre en doute les effets bienfaisants de ce produit sur leurs collections.

Entouré d'une telle aura, le gel de silice bleu, blanc ou rose, se trouve distribué plus ou moins généreusement dans les vitrines des musées et même parfois dans les bureaux des conservateurs. La plupart du temps quelques grains éparpillés dans une soucoupe placée au pied de "l'objet à protéger" suffisent à donner bonne conscience aux responsables.

Tout ceci évidemment découle d'un manque de connaissance

des problèmes de contrôle du climat, des façons de contrôler celui-ci, du climat nécessaire à la bonne conservation d'un certain type de collection et enfin du comportement du gel de silice.

Pourtant, d'excellents articles théoriques [1,2,3,4] ont démontré l'importance du gel de silice. D'autres articles ont indiqué des réalisations concluantes [5 - 10]. Il semble que ces articles ne soient pas arrivés jusqu'aux conservateurs ou que les côtés techniques de ces articles aient rebuté les responsables des collections. J'essayerai donc d'éviter cet écueil, quitte à paraître, pour les initiés, parfois un peu simpliste dans l'exposé qui va suivre.

1. Réaction des collections face à l'air humide

Il faut clairement définir 2 types de collections:

- les collections en bois, papier, tissus, peau, cuir, parchemin, ivoire, que nous appellerons "organiques".
- les collections en métal, verre, céramique, pierre, que nous appellerons "inorganiques".

Les collections organiques sont formées de matériaux qui, s'ils sont secs et entourés d'air humide, sont capables d'absorber sous forme de vapeur une partie de la vapeur d'eau contenue dans l'air environnant jusqu'à se trouver en *équilibre* avec les conditions ambiantes. En s'humidifiant ainsi, les objets augmentent de poids et se gonflent.

De même, si ces produits sont humides et entourés d'air plus sec, ils fourniront de la vapeur d'eau à l'air environnant jusqu'à ce qu'un nouvel *équilibre* se produise. En se séchant ainsi, les objets perdront du poids et risqueront de se fendre.

Quelque soit l'âge des collections organiques, l'échange de vapeur d'eau entre l'objet et l'air environnant se poursuit sans interruption entraînant des mouvements de la matière. De ce fait, les collections organiques craindront avant tout les variations d'humidité dans l'air.

Les collections inorganiques réagissent d'une manière plus complexe en présence d'eau mais l'on peut dire qu'en règle générale, elles craignent l'air humide et parfois les variations d'humidité.

2. Valeurs à contrôler: température et humidité relative

La température dans une vitrine varie durant une journée. Ceci est dû à la circulation d'air, à la présence de l'éclairage, au chauffage central et à la présence des visiteurs. Ces variations ne peuvent pas dans la plupart des cas être diminuées. Au mieux, elles peuvent être réduites.

Les variations de température (5°C à 35°C) vont entraîner de faibles variations dimensionnelles de l'objet (spécialement dans le cas des objets organiques) mais ON NE REPETERA JAMAIS ASSEZ QUE LES VARIATIONS D'HUMIDITE RELATIVE (0% à 100%) ENTRAINENT DES VARIATIONS DIMENSIONNELLES DE L'OBJET BEAUCOUP PLUS IMPORTANTES QUE CELLES CAUSEES PAR LES VARIATIONS DE TEMPERATURE.

Pour la bonne conservation des collections, il sera donc essentiel de contrôler avant tout l'humidité relative.

L'humidité relative⁽¹⁾ est un facteur moins évident que la température. Il faut savoir cinq choses:

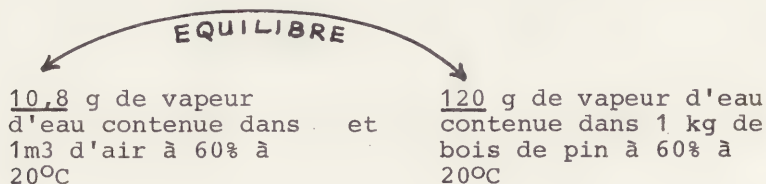
- dans un volume clos, quand la température croît, l'humidité relative de l'air décroît;
- dans un volume clos, quand la température décroît, l'humidité relative croît;
- dans un volume clos, pour augmenter l'humidité relative, il faut:
 - ou abaisser la température
 - ou ajouter de la vapeur d'eau;
- dans un volume clos, pour diminuer l'humidité relative, il faut:
 - ou augmenter la température
 - ou enlever de la vapeur d'eau;
- si nous voulons maintenir stable l'H.R., il faut:
 - ajouter de la vapeur d'eau quand la température augmente;
 - enlever de la vapeur d'eau quand la température diminue.

3. Comment les collections organiques sont-elles en équilibre avec l'air environnant ?

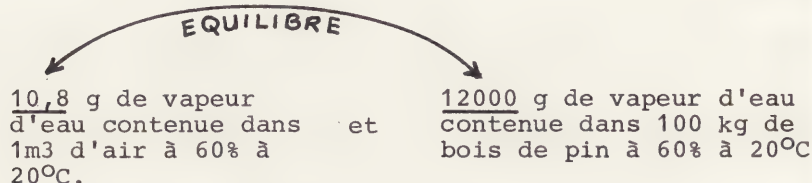
Prenons un objet organique qui se trouve depuis une semaine dans une vitrine ayant une humidité relative stable. Il se mettra naturellement en *équilibre* avec l'air environnant.

A titre d'exemple, à 20°C, un mètre cube d'air à H.R.=60%

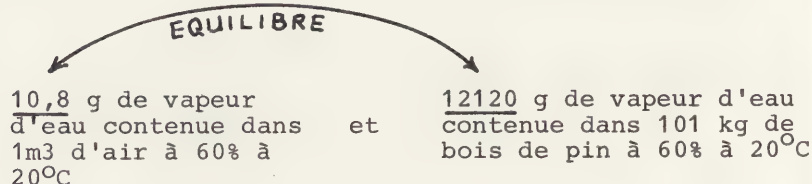
contient 10,8 g de vapeur d'eau, et à 20°C et à 60% H.R., un kilo de bois contient 120 g de vapeur d'eau. Mis en contact, nous aurons l'équilibre suivant:



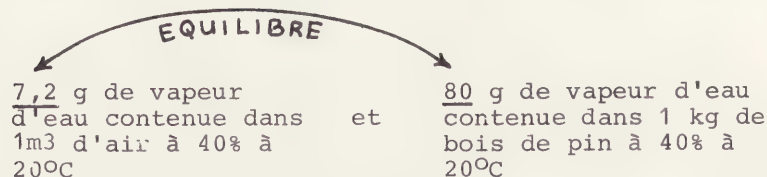
Comme nous aurons l'équilibre suivant:



Comme nous aurons l'équilibre suivant:



Par ailleurs, à 20°C un mètre cube d'air à H.R. = 40% contient 7,2 g de vapeur d'eau, et à 20°C et H.R. = 40%, un kilo de bois de pin contient 80 g de vapeur d'eau. Mis en contact, nous aurons l'équilibre suivant:



Dans tous les cas précédents, il y a équilibre. A première vue, ce sont des équilibres bien déséquilibrés mais la nature est ainsi faite.

Ainsi donc dans une vitrine contenant un objet organique en équilibre avec l'humidité de l'air environnant, si cette humidité relative diminue (l'air va sécher), l'équilibre entre la quantité de vapeur d'eau contenue dans l'objet et la quantité de vapeur d'eau dans l'air est rompu; l'objet fournira de la vapeur d'eau à l'air jusqu'à ce que se réalise un nouvel équilibre. Durant la désorption de vapeur d'eau l'objet risque de se fendre. Réciproquement, dans une vitrine contenant un objet organique en équilibre avec l'humidité de l'air environnant, si l'H.R. augmente (l'air s'humidifie) l'équilibre entre la quantité de vapeur d'eau contenue dans l'objet et la quantité de vapeur d'eau contenue dans l'air est rompu; l'objet absorbera de la vapeur d'eau de l'air humide jusqu'à ce que se réalise un nouvel équilibre. Durant l'absorption de la vapeur d'eau, l'objet se gonflera avec les risques de détérioration décrits plus haut.

On voit donc que si dans une vitrine l'humidité relative varie - et elle varie - les objets organiques contenus dans cette vitrine donnent ou absorbent de la vapeur d'eau de l'air.

Il faudrait éviter ces échanges. Ceci est possible en utilisant des produits dont le pouvoir de donner ou d'absorber de la vapeur d'eau est plus grand que celui des collections organiques. Ces produits, qui vont éviter que les variations d'humidité de l'air soient ressenties directement par les collections, s'appellent matériaux-tampon.

4. Comparaison simple entre un matériau-tampon dans une vitrine et un barrage sur une rivière

Sur une rivière toute variation du niveau de l'eau en amont est repercutée plus ou moins rapidement en aval. Dans un musée toute variation d'humidité relative à l'extérieur de la vitrine est repercutée plus ou moins rapidement à l'intérieur de celle-ci.

Un matériau-tampon dans une vitrine a le même rôle qu'un barrage sur une rivière.

Le barrage a pour but de maintenir le niveau d'eau en aval constant quelles que soient les variations en amont. Le matériau-tampon a pour but de maintenir dans une vitrine le niveau d'H.R. constant quelles que soient les variations à l'extérieur.

Si le niveau de la rivière baisse en amont du barrage, on ouvrira les vannes du barrage pour éviter une baisse de niveau en aval. Plus le barrage est grand, plus longtemps le niveau en aval restera constant. Le barrage prendra à son compte le déficit d'eau dû à l'assèchement de la rivière en amont.

Si l'H.R. baisse à l'intérieur d'une vitrine, le matériau-tampon donnera de l'humidité qu'il contient à l'air dans la vitrine pour éviter qu'elle ne s'assèche. Plus la quantité de matériau-tampon est grande, plus longtemps l'humidité relative dans la vitrine restera constante. Le matériau-tampon prend sur lui le déficit de vapeur d'eau dû à l'assèchement de l'air.

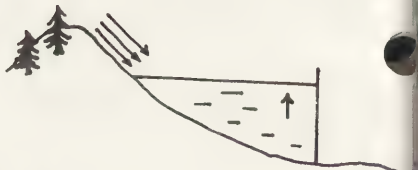
Si le niveau de la rivière monte en amont du barrage, le barrage en fermant ses vannes absorbera cet excès pour éviter une montée du niveau en aval. Plus le barrage est grand, plus longtemps le niveau en aval restera constant. Le barrage prendra sur lui l'excédent d'eau dû à la montée de la rivière en amont.

Si l'H.R. monte à l'intérieur d'une vitrine, le matériau-tampon absorbera l'excès d'humidité pour éviter à l'air de la vitrine de s'humidifier. Plus la quantité de matériau-tampon est grande, plus longtemps l'humidité relative dans la vitrine restera constante. Le matériau-tampon prendra sur lui l'excédent de vapeur d'eau dû à l'air humide.

Fig. 1

Rivière sans barrage

Rivière avec barrage



Nous pouvons dire qu'un barrage a pour but de stabiliser le cours d'une rivière comme un matériau-tampon a pour but de stabiliser l'humidité relative dans une vitrine.

5. Comment classer les matériaux-tampon ?

Le bois, le papier, le tissu, l'argile sont des matériaux-tampon. Prenons, par exemple, 1m³ de papier journal sec. Son poids sera de 535 kilos. Augmentons l'humidité de l'air. Le papier absorbera de l'humidité et augmentera de poids. En partant avec 1m³ de papier, on obtiendra les valeurs suivantes:

poids de vapeur d'eau contenue dans 1m ³ d'air à 20°C	H.R.	poids de vapeur d'eau contenue dans 1m ³ de papier à 20°C
0 gramme	0%	0 kilo
8,5 grammes	50%	55 000 grammes
15,4 grammes	90%	148 000 grammes

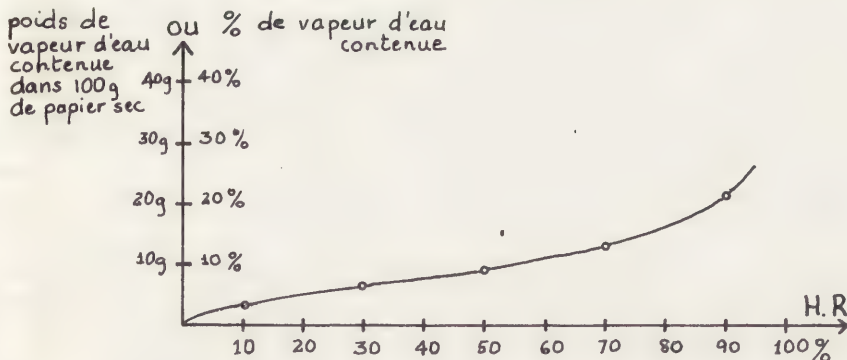
A chacune de ces humidités, si le mètre cube d'air est mis en contact avec le m³ de papier, il y aura *équilibre*.

C'est à dire, par exemple, qu'à 50% d'humidité relative, 8,5 g/m³ de vapeur d'eau contenue dans l'air sont en *équilibre* avec les 55 kilos de vapeur d'eau contenue dans le papier.

Pour le papier journal, il sera possible de tracer la courbe d'augmentation du poids - ou ce qui est identique, le % de vapeur d'eau contenue - en fonction de l'augmentation d'H.R.

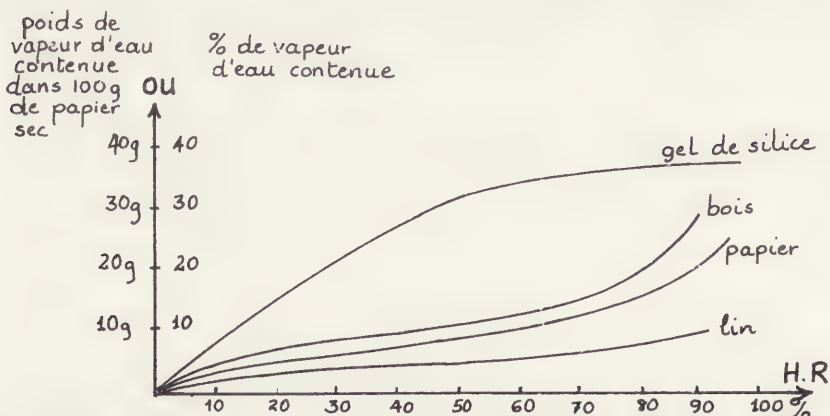
On obtient une courbe de ce type.

Fig. 2



Une courbe identique peut être tracée pour d'autres types de matériau-tampon [2].

Fig. 3



Le meilleur matériau-tampon sera celui qui aura la plus grande capacité à absorber de la vapeur d'eau. A la vue du graphique n° 3, il est évident que le meilleur matériau-tampon est le gel de silice. Voilà pourquoi il est recommandé pour aider à stabiliser le climat dans les musées.

6. Le gel de silice: fiche technique

Formule : SiO_2

Nom chimique : Silice - le gel de silice est une des trois variétés cristallines de la silice (une autre est le cristal de roche).⁽⁵⁾

Aspect : Solide cristallin normalement incolore. On trouve dans le commerce du gel de silice "avec indicateur coloré". La coloration est donnée par une faible quantité de sel de cobalt. Ce produit est bleu lorsque l'humidité relative est comprise entre 0% et 20%. Le produit est rose quand l'humidité relative est comprise entre 30% et 100%.

Couleur du gel de silice

NORMAL
AVEC
INDICATEUR

0% blanc — 20% blanc — 30% blanc — 100%
bleu mauve rose

Le gel de silice avec indicateur n'est utile que si l'on désire créer une H.R. inférieure à 20%. Il n'a aucun avantage pour créer une H.R. comprise entre 30 et 100%.

La taille des cristaux varie de 0,10mm à 6mm de diamètre. Pour les musées, il est préférable de ne pas utiliser des cristaux trop fins qui se pulvérisent plus facilement.

Prix : de gros ϕ 3 - ϕ 5 le kilo.

Propriétés : Corps très stable, indécomposable chimiquement par la chaleur.

Inattaquable par les micro-organismes.

Absorbe et rejette de la vapeur d'eau suivant les conditions hygrométriques de l'air ambiant.

Cherche toujours à avoir son contenu de vapeur d'eau en *équilibre* avec la vapeur d'eau contenue dans l'air.

Peut absorber jusqu'à 40% de son poids de vapeur d'eau, c'est-à-dire, qu'un kilo de gel de silice sec peut absorber 400 g de vapeur d'eau.

Reste apparemment sec même lorsque l'H.R. est de 100%.

Peut être équilibré à toutes les humidités relatives allant de 0% à 100%.

Dans un volume fermé, le gel de silice impose pendant un temps plus ou moins long l'humidité relative avec laquelle il a été équilibré. On équilibre le gel de silice à l'H.R. voulue en l'exposant dans une ambiance ayant l'H.R. choisie pendant une période assez longue (qui peut aller jusqu'à une semaine).

Usage musée : Il stabilise un air à H.R. variable.
Sec, il dessèche un air humide.
Humide, il humidifie un air sec.

Usage général : Dessicant pour fabricants du matériel électronique et militaire, et pour le transport du matériel craignant l'humidité.

7. Le gel de silice comme stabilisateur d'humidité relative

Divers musées ont stabilisé l'humidité relative dans leurs vitrines de cette manière:

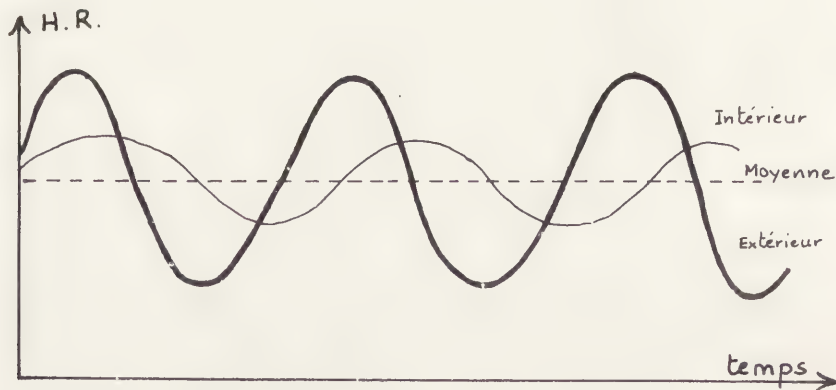
- La Galerie Nationale du Canada pour un triptyque de di Cione et un panneau de Simone Martini [6]. L'H.R. qui varie dans la galerie de 30 à 55% est stabilisée à 45 - 50%.
- Le Palais Pitti à Florence pour 184 instruments à corde provenant du Conservatoire de Musique Luigi Cherubini [11]. L'humidité extérieure varie de 28% à 72%. Dans les vitrines l'H.R. est stable à 52 - 54%.
- Le Corning Museum of Glass à Corning, N.Y. [9] pour maintenir une H.R. de 42% autour d'une collection de verres fragiles.
- Le Musée d'Art et d'Histoire de Genève [8] dans deux vitrines contenant des icônes durant une exposition temporaire. L'H.R. extérieure variait de 44 à 74% tandis que l'H.R. intérieure était maintenue à 58 - 60%.

Comment le gel de silice peut-il stabiliser l'H.R. ?

Supposons un musée contenant des objets organiques et ne possédant pas de système d'air conditionné ou possédant un système d'air conditionné fonctionnant mal. Une vitrine bien construite diminuera et retardera les variations d'hygrométrie extérieures.

L'humidité relative variera ainsi.

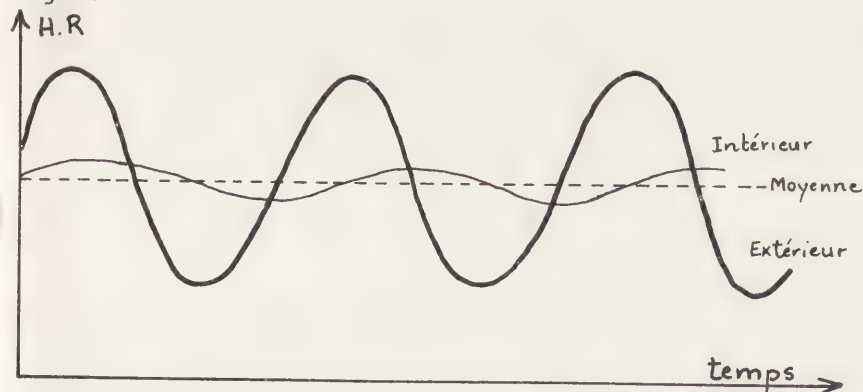
Fig. 4



Plus la vitrine sera hermétique, plus les variations d'humidité relative seront diminuées ou retardées.

Avec un matériau-tampon dans la vitrine l'humidité relative variera ainsi.

Fig. 5



Plus il y aura de matériau-tampon, plus les variations d'humidité relative seront diminuées et retardées.

Cette quantité dépend de 3 facteurs :

- L'étanchéité de la vitrine⁽²⁾. Si la vitrine est peu hermétique, l'air extérieur pénétrera rapidement et le gel de silice se mettra en *équilibre* avec l'air extérieur.
- La différence entre l'H.R. à l'extérieur de la vitrine et l'H.R. à l'intérieur de la vitrine. Plus cette différence est grande, plus l'H.R. intérieure aura tendance à rejoindre l'H.R. extérieure et plus il faudra mettre de gel de silice.
- Le volume de la vitrine. Plus la vitrine est grande, plus il faudra mettre de gel de silice.

Dans un musée dont le climat est parfois trop sec et parfois trop humide pour les collections organiques, le gel de silice sera utilisé ainsi :

- Dans une vitrine bien close.
- Au contact de l'air dont l'H.R. est à stabiliser.
- En quantité suffisante. Garry Thomson préconise une quantité de 20 kg/m³. Ceci peut paraître beaucoup et certains s'y refuseront à cause du prix. En fait,

le coût est minime par rapport au coût total d'une vitrine. Par ailleurs, à long terme, le gel de silice évitera des détériorations et des restaurations beaucoup plus coûteuses.

- d) Avec un hygromètre pour contrôler l'H.R. dans la vitrine.
- e) Dans les conditions adéquates décrites plus haut il n'y a besoin d'AUCUNE MANIPULATION.

8. Le gel de silice comme déshumidificateur

Divers musées ont déshumidifié l'air dans leurs vitrines de cette manière et, par exemple,

- Le Musée archéologique d'Amman pour un rouleau de bronze corrodé provenant de Qumran. L'humidité relative moyenne annuelle est de 61%. A l'intérieur de la vitrine, l'H.R. est maintenue inférieure à 20%.
- Au Japon, lors de l'exposition de la Joconde⁽⁴⁾, l'H.R. fut maintenue à 55% alors qu'à l'extérieur l'H.R. était de 70% [7].

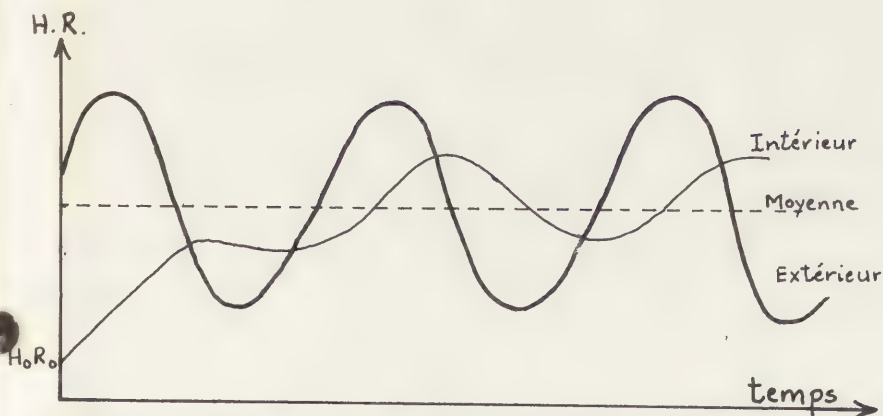
Cet usage du gel de silice est le plus courant. Le produit est employé ainsi pour maintenir un air sec dans les emballages d'appareil de photos neufs et quelquefois en pharmacie ou en confiserie. Cet usage est aussi bien connu des chimistes.

Dans ce cas, le gel de silice préalablement séché (c'est-à-dire, mis en *équilibre* avec une H.R. inférieure) absorbe la vapeur d'eau contenue dans l'air humide jusqu'à se trouver en *équilibre* avec l'H.R. de l'air environnant. A partir de ce moment-là, le gel de silice ne joue plus le rôle de déshumidificateur mais de stabilisateur. Pour qu'il serve à nouveau de déshumidificateur, il faut le régénérer, c'est-à-dire, le sécher. On réalisera ceci en le mettant au contact d'un air sec à qui le gel de silice donnera la vapeur d'eau qu'il a précédemment emmagasiné⁽³⁾.

Supposons une vitrine contenant des objets métalliques nécessitant une humidité relative basse.

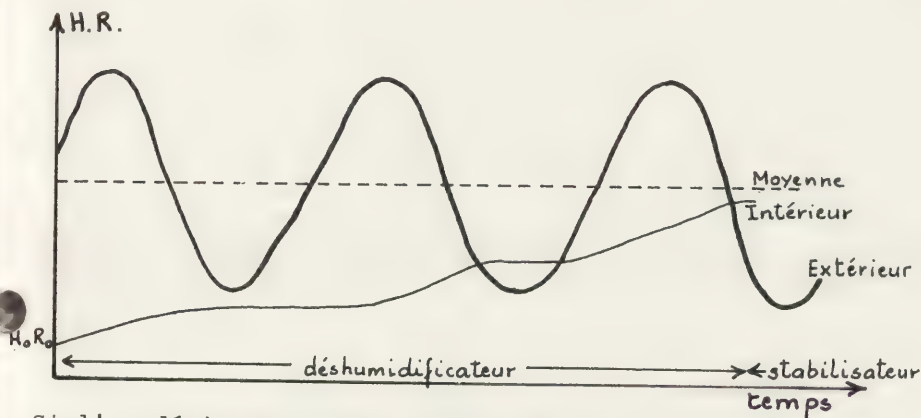
Imaginons que l'on parvienne à mettre un air bien sec à l'H.R. idéale H_0R_0 dans la vitrine. Ces conditions idéales de conservation ne se maintiendront malheureusement pas car aucune vitrine n'est parfaitement hermétique. Avec le temps, on obtiendrait une augmentation de l'H.R. dans une vitrine, augmentation plus ou moins rapide suivant que la vitrine est plus ou moins étanche (fig. 6).

Fig. 6



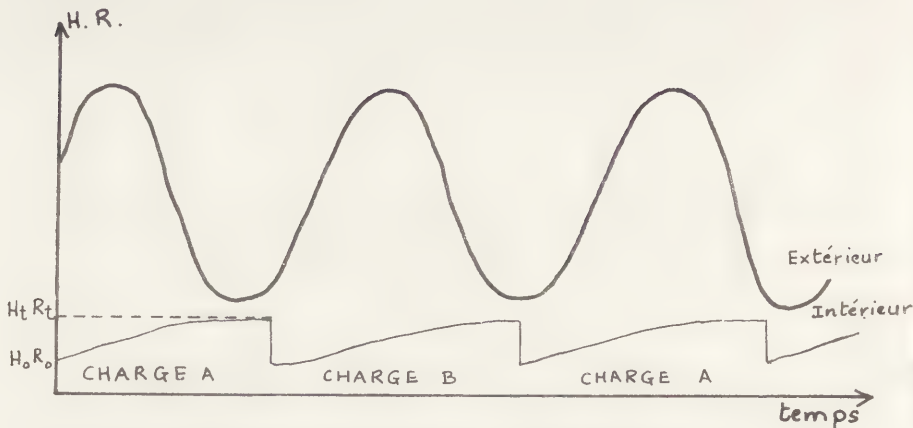
Avec une charge de gel de silice préalablement équilibré à H_0R_0 , l'augmentation de l'H.R. dans la vitrine sera beaucoup plus lente (fig. 7). Le gel de silice absorbera lentement de la vapeur d'eau jusqu'au moment où, ayant atteint l'équilibre avec l'humidité de l'extérieur de la vitrine, il jouera le rôle de stabilisateur.

Fig. 7



Si l'on désire maintenir l'H.R. dans la vitrine à un niveau inférieur à valeur choisie proche de H_0R_0 , il sera nécessaire d'utiliser deux charges (A et B) de gel de silice (fig. 8). Lorsque la charge A qui est dans la vitrine est en train d'absorber de la vapeur d'eau, la charge B est à l'extérieur pour régénération à H_0R_0 . Lorsque l'humidité relative dans une vitrine atteint le seuil maximum tolérable H_{tR_t} , on échange les charges A et B. Et ainsi de suite.

Fig. 8



La quantité à utiliser dépend de 4 facteurs:

- L'étanchéité de la vitrine. Si la vitrine est peu étanche, l'air de l'extérieur y pénétrera rapidement et le gel de silice se mettra en *équilibre* avec l'H.R. extérieure et jouera alors le rôle de stabilisateur.
- La différence entre l'H.R. à l'extérieur de la vitrine et l'H.R. à l'intérieur de la vitrine. Plus cette différence est grande, plus l'H.R. à l'intérieur aura tendance à rejoindre les conditions extérieures et plus il faudra mettre de gel de silice.
- Le volume de la vitrine. Plus la vitrine est grande, plus il faudra mettre de gel de silice.
- La fréquence de manipulation: moins souvent le conservateur désirera échanger les charges de gel de silice, plus celles-ci devront être importantes.

Dans un climat toujours trop humide pour les collections, le gel de silice sera donc utilisé ainsi:

- Le plus souvent pour diminuer l'H.R. autour des collections métalliques⁽³⁾;
- dans une vitrine bien close;
- au contact de l'air dont l'H.R. est à diminuer;
- deux charges A et B de gel de silice sont nécessaires.
- Si l'on utilise le gel de silice incolore, un hygromètre est nécessaire pour établir le moment d'échanger les charges A et B. Si l'on désire maintenir une

H.R. inférieure à 20%, il est conseiller d'utiliser du gel de silice avec indicateur coloré. Au moment où celui-ci virera du bleu au rose, il faudra échanger les charges.

- f) Pour éviter des manipulations trop fréquentes, ne jamais mettre moins d'un kilo de gel de silice par m³ de vitrine.

9. Le gel de silice comme humidificateur

Divers musées dont le climat est trop sec, humidifient leurs vitrines au moyen de gel de silice. Par exemple:

- Le Sainsbury Centre for Visual Arts pour des statues en bois d'art africain. L'H.R. est maintenue à 55% quand l'H.R. extérieure moyenne annuelle se situe aux environs de 40% [10].
- Le Musée des Beaux Arts de Montréal pour la collection de dessins et d'estampes. H.R. = 50% quand l'H.R. extérieure varie de 20% à 42% [6].
- Le Los Angeles County Museum of Art [5] pour un tableau sur bois de Rembrandt. H.R. = 60% quand l'H.R. extérieure était de 52%.

Cet usage du gel de silice est le moins commun et certainement celui qui demande le plus de travail et d'attention de la part du responsable. Il sera appliqué quand un objet organique habitué à un climat humide (H_oR_o) est exposé dans un musée ayant un climat sec.

Imaginons que l'on parvienne à créer dans la vitrine l'humidité relative (H_oR_o) à laquelle l'objet était habitué. Ces conditions idéales de conservation ne se maintiendront malheureusement pas car aucune vitrine n'est parfaitement hermétique.

Avec le temps on obtiendrait une diminution de l'H.R. dans la vitrine, diminution plus ou moins rapide suivant que la vitrine est plus ou moins étanche (fig. 9).

Avec une charge de gel de silice préalablement équilibré à H_oR_o , la diminution de l'H.R. dans la vitrine sera beaucoup plus lente (fig. 10). Le gel de silice donnera lentement de la vapeur d'eau jusqu'au moment où, ayant atteint l'équilibre avec l'H.R. moyenne à l'extérieur de la vitrine, il jouera le rôle de stabilisateur.

Fig. 9

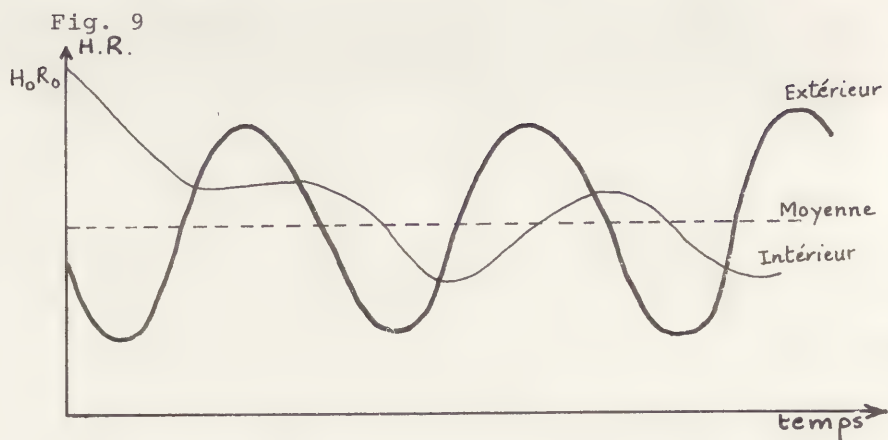


Fig. 10

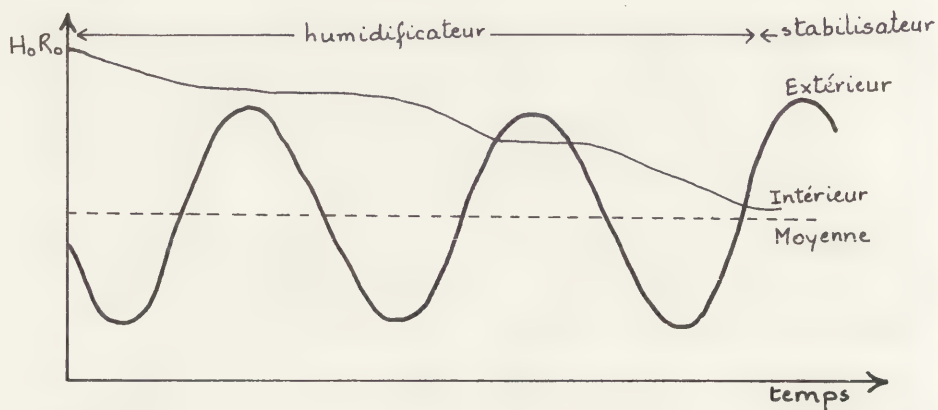
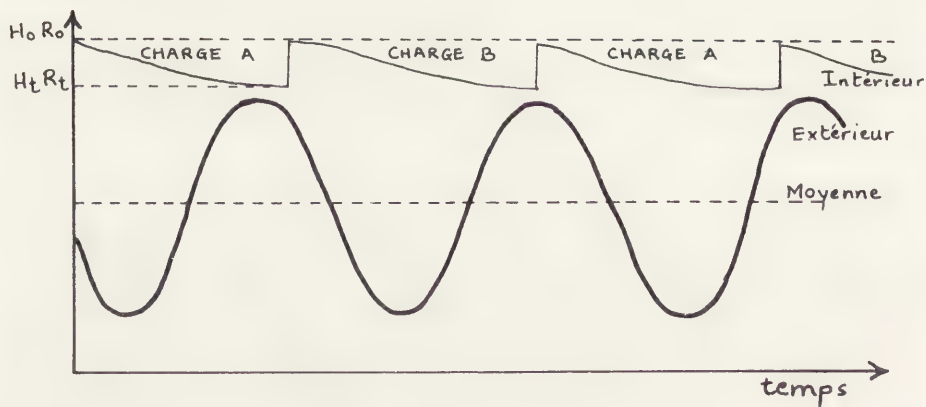


Fig. 11



Si l'on désire maintenant maintenir l'H.R. dans la vitrine à un niveau supérieur à une H.R. minimum toléré (H_{tR_t}), il sera nécessaire d'utiliser 2 charges (A et B) de gel de silice (fig. 11). Lorsque la charge A est dans la vitrine en train de fournir de la vapeur d'eau, la charge B est à l'extérieur pour être réhumidifiée et mise en équilibre avec l' H_oR_o voulue. Lorsque l'humidité relative dans la vitrine a atteint le seuil minimum toléré H_{tR_t} , on échange les charges A et B. Et ainsi de suite.

La quantité à utiliser dépend de 5 facteurs:

- a) L'étanchéité de la vitrine. Si la vitrine est peu étanche, l'air de l'extérieur pénétrera rapidement et le gel de silice se mettra en équilibre avec l'H.R. extérieure et jouera alors le rôle de stabilisateur.
- b) La différence entre l'H.R. à l'extérieur de la vitrine et l'H.R. à l'intérieur de la vitrine. Plus cette différence est grande, plus l'H.R. de l'intérieur aura tendance à rejoindre les conditions extérieures et plus il faudra mettre de gel de silice.
- c) Le volume de la vitrine. Plus la vitrine est grande, plus il faudra mettre de gel de silice.
- d) La fréquence de manipulation. Moins souvent le conservateur désirera échanger les charges de gel de silice, plus celles-ci devront être importantes.
- e) La différence entre H_oR_o et l'humidité relative minimum tolérée (H_{tR_t}).

Dans un climat toujours trop sec pour des collections organiques, le gel de silice sera utilisé ainsi:

- a) pour augmenter l'humidité relative autour d'un objet;
- b) dans une vitrine bien close;
- c) au contact de l'air dont l'H.R. est à augmenter.
- d) 2 charges A et B de gel de silice sont nécessaires.
- e) Il est inutile de prendre de gel de silice avec indicateur. Par contre, il est nécessaire d'avoir dans la vitrine un hygromètre pour établir le moment d'échanger les charges A et B.
- f) Pour éviter des manipulations trop fréquentes ne jamais mettre moins d'un kilo de gel de silice par mètre cube de vitrine.

Conclusion

Le gel de silice peut apporter une aide considérable aux responsables désirant contrôler le climat dans un petit espace clos (maximum 4-5m³), afin de préserver des collections contre une humidité relative inadéquate ou contre des variations d'humidité relative. Cependant il est essentiel de savoir utiliser le produit et d'avoir prévu des vitrines adaptées à son utilisation. Le coût d'achat peut paraître prohibitif mais à long terme - le produit garde toujours ses qualités - le contrôle du climat au moyen de gel de silice s'avère une méthode très sûre, simple et d'un coût minimum à l'entretien.

Notes

(1) L'air absorbe de la vapeur d'eau. Lorsque l'air ne peut plus absorber de vapeur, on dit qu'il est saturé. La valeur de la saturation augmente avec la température.

L'H.R. est le rapport entre la quantité de vapeur d'eau contenue dans un mètre cube d'air à la quantité maximum de vapeur d'eau ce même mètre cube pourrait contenir à saturation à la même température. Si l'H.R. est, par exemple, de 60%, cela signifie qu'à cette température l'air contient 60% du total de la vapeur d'eau qu'il pourrait contenir s'il était saturé.

(2) Il est nécessaire de préciser ici qu'il n'existe pas de vitrine dans laquelle on puisse faire le vide. Par ailleurs, quelles que soient les précautions prises, il y a toujours des échanges d'air entre l'intérieur et l'extérieur de la vitrine.

(3) Si l'on désire complètement assécher de l'air, on mettra au préalable le gel de silice dans une étuve à 110°C ou même un four de cuisine durant une heure. Cependant, en plein été à Bagdad à midi (H.R. = 8%), il est possible de régénérer du gel de silice humide en une demi-heure en l'exposant au soleil.

(4) Dans ce cas, un autre produit tampon appelé Zeolite fut employé.

(5) Le gel de silice est un produit de l'industrie chimique. A part quelques fabricants au niveau national, le plus gros fabricant au niveau mondial est: W.R. Grace & Co., Davison Chemical Division, P.O. Box 2117, Baltimore, MD 21203, U.S.A., Tél: (301) 727 3900 et 659 9000, Tx:090801. Cette maison fabrique plus de 20 types de gel de silice dont 7 types normaux blancs de grosseurs différentes (de 0,2mm à 4mm) et 7 types avec indicateur coloré. Le produit est toujours fourni équilibré avec une H.R. inférieure à 1%.

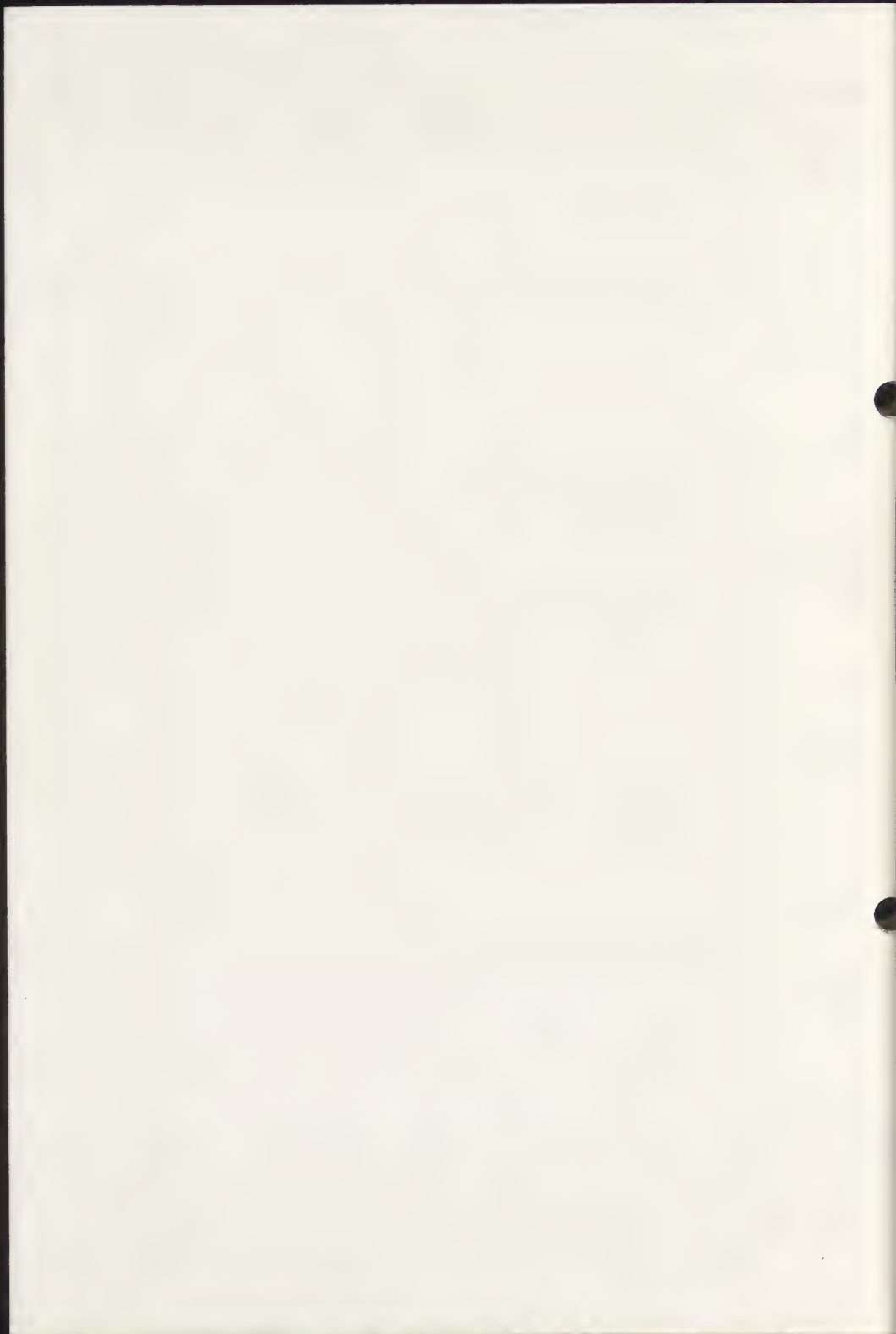
Références

Théorie & recherche

- [1] Thomson, Garry - Relative Humidity - Variation with Temperature in a Case containing Wood, Studies in Conservation IV (1964), pp. 153-169.
- [2] Stolow, Nathan - Fundamental Case Design for Humidity Sensitive Collections, Museum News, technical supplement (Février 1966), n° 11, pp. 45-52.
- [3] Thomson, Garry - Stabilization of R.H. in Exhibition Cases : Hygrometric Half-time, Studies in Conservation 22 (1977), pp. 85 - 102.
- [4] Weintraub, Steven - A New Design for a Low Maintenance Silica Gel System for the Control of Relative Humidity in a Sealed Case. Preprints of IIC Conference in Vienna (Septembre 1980) pp. 55-56.

Réalisation

- [5] Johnson, B.B., Cairns, T. - Art Conservation and Analysis, Analytical Chemistry, Vol. 44 (1972) pp. 26A - 27A.
- [6] Stolow, Nathan - The Microclimate : a Localized Solution, Washington D.C., Museum News, Vol. 56, n° 2 (Nov-Déc. 1977), pp. 57-63.
- [7] Miura, Sadatoshi - Control of Climate in a Showcase by means of Zeolite - Report on Exhibition of La Joconde. Communication de la conférence de l'ICCRUM sur le climat dans les musées, Rome (Nov. 1979), pp. 1-15.
- [8] Schweizer, François & Rinvy, Anne - Zur Mikroklimateisierung zweier Vitrinen mit Ikonen für eine temporäre Ausstellung, Maltechnik, No 4 (Oct. 1980) pp. 239-243.
- [9] Brill, Robert H. - The Use of Equilibrated Silica Gel for the Protection of Glass with Incipient Crizzling, Journal of Glass Studies, Vol. 20 (1978), pp. 100-118.
- [10] Ramer, Brian - Stabilizing R.H. within Display Cases: the Role of Silica Gel and Case Design. Preprints of ICOM Conservation Committee, Ottawa, Working Group on Climate and Lighting Control (Sept. 1981).
- [11] de Guichen, Gaël & Gai, Vincio - Contrôle du climat autour de 200 instruments de musique (publication en cours).



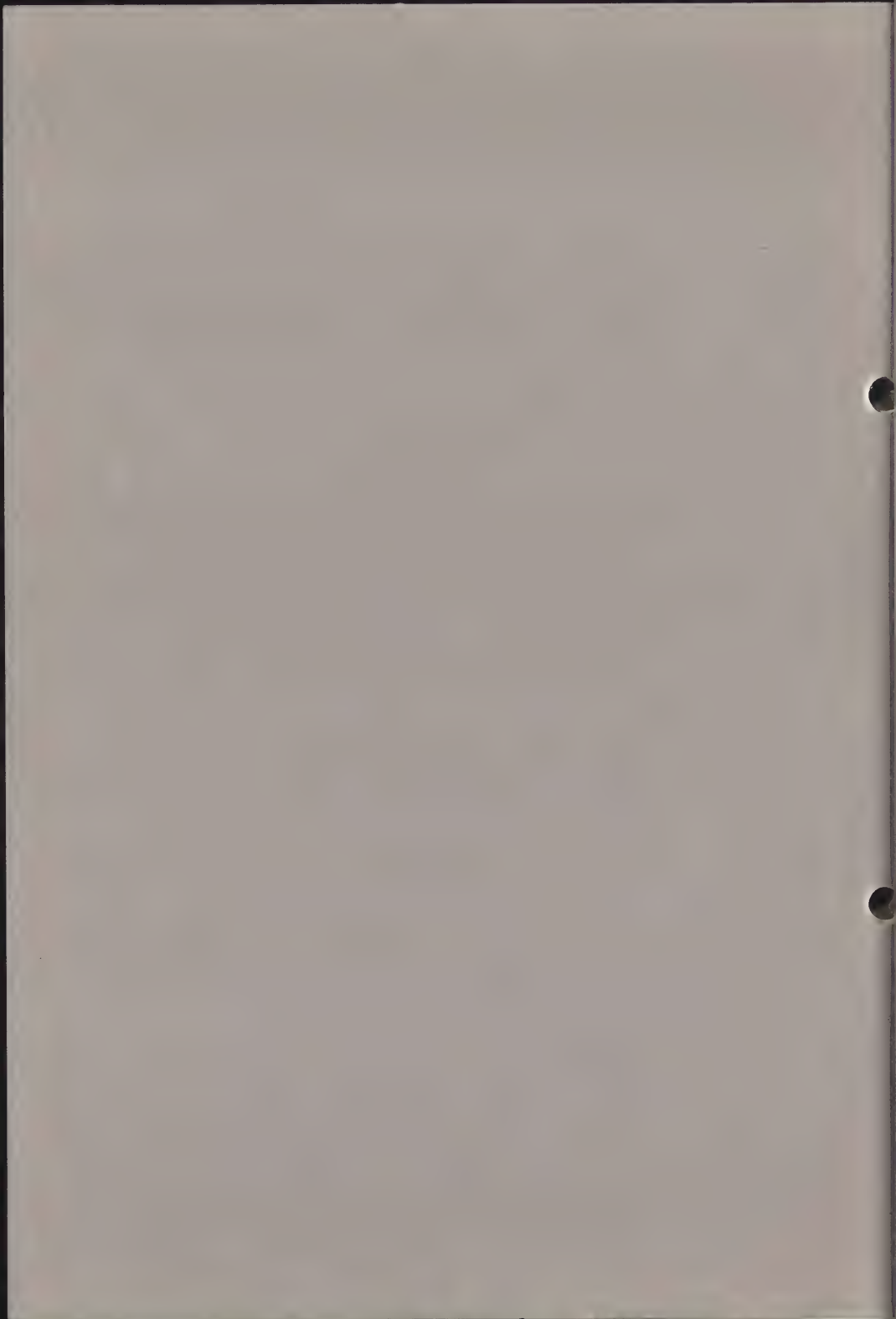
81/18/8

CONTROLLED CLIMATE CASES FOR WORKS OF ART:
INSTALLATION AND MONITORING

Nathan Stelow

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting



CONTROLLED CLIMATE CASES FOR WORKS OF ART: INSTALLATION
AND MONITORING

Nathan Stelow

Conservation Consultant Works of Art
P.O.Box 2542 Station D
Ottawa, Ontario K1P 5W6
Canada

Abstract

Further experiences in museums and art galleries are reported on the use of conditioned silica gel for the buffered control of relative humidity within specially designed cases. Recent projects are described: the case enclosure of a very large panel painting by Neri di Bicci, an early Irish Harp (featured in the Early Irish Treasures Exhibition) and a variety of important ethnographic treasures, such as a Benin bronze. The method of selection of the silica gel presentation system is discussed for each installation. Also described are the holding devices, method of case closure, and monitoring instruments for recording the relative humidity. Of the latter the most practical ones are also the least expensive, i.e., cobalt strip indicators. In museum situations it is necessary to develop case designs which are trouble-free for very long periods of time, and which have the least problems with monitoring and calibration of instruments.

The first project described is the enclosure of the large Neri di Bicci panel painting and its predella in an acrylic case with a gasketted removable back. The dimensions of the Painting with its predella are: 2.28 m high (left), 2.30 m (centre height), 2.30 m (right), width at top 2.345 m, and at bottom 2.16m. The thickness at the maximum position (bowing of the panel and the framing elements) was approximately 0.24 m. The weight overall was estimated to be 250 Kg. The acrylic case designed for enclosing the painting was of massive construction to be sufficiently rigid to avoid optical distortions on the front viewing surface, and to permit the attachment of the back access panel in a very firm manner. It was decided to construct the acrylic case of dimensions slightly larger overall so that the buffering action of the silica gel would be as effective as possible. Thus the relatively small air volume to "object" volume was planned for

this purpose. The case dimensions were: 2.55 m high, 2.54 m wide, and 0.36 m deep (all outside dimensions). The acrylic sheets were 1.2 cm stock ($\frac{1}{2}$ inch) and had to be specially cast by the factory as they were beyond the standard dimensions. The pedestal supporting the case (the case weighed about 450 Kg empty) was made of wood and laminate coating of slightly larger width and length so as to provide a perimeter ledge; its height 0.52 m off the ground.

On the basis of the geometry and weight of the Neri di Bicci panel painting and the internal supporting materials, fabrics, wood, etc., it was decided that it would be necessary to place inside the case in some suitable manner about 200 Kg of conditioned silica gel. After careful consideration it was decided, as in previous analogous installations, that this amount of silica gel should be most effective in moisture transfer within the high case, without too much of a gradient in R.H.; if a vertical wall were installed at the back. This took the form of a screened panel of strong construction, covered with pleasing fabric (linen), and fixed to the removable back plate of the case. The silica gel panel was a unit in itself and could be readily unscrewed from the back panel for servicing or reconditioning if necessary.

On the basis of the past environmental history of the painting it was decided to establish a slightly higher than average R.H. within the case, i.e., 45%. The large amount of silica gel was conditioned to this level by utilizing a specially designed conditioning chamber with a controllable domestic-type humidifier as the "charging" device. Equilibrium moisture content tests were carried out periodically during the conditioning process to establish via sorption curves (isotherms) that the 45% operating level was reached. An excess beyond the 200Kg required was prepared in this manner for stand-by use. For monitoring the interval case R.H. thought was given to electronic probes, or other devices. However these require frequent calibration, tend to drift, and are costly. Since excellent experience has been had with cobalt salt paper card indicators these were installed in the case one on each side. After one year of operation the internal R.H. has remained fairly constant between 40-43% R.H., notwithstanding wide variations in the gallery climate.

The second 'case' concerns the installation in a climate controlled case of an early Irish Harp, one of the principal exhibits of the Early Irish Treasures Exhibition which circulated in the U.S.A. in 1977-79 (along with such world treasures as the Book of Kells, and the Ardagh Chalice). The Harp required a controlled environment close to 55% at all times. However this was difficult to achieve given the nature of the case and pedestal design. The pedestal was not isolated from the upper vitrine, and

taken together, the combined volume was larger than necessary for effective control by a buffering agent such as conditioned silica gel. In the initial design it was suggested that the gel be placed on a tray at the very bottom of the pedestal! This would not work given the great distance from the Harp, and the obstruction of the supporting platform for the Harp. The conservation consultant requested that the case be redesigned with the platform being raised to allow for clear air passage to the lower space, and that the silica gel be brought right up to the level of the platform itself. It was also necessary to eliminate the lower pedestal space as being unnecessary air volume.

It was suggested too that a more effective solution would have been to present the gel in a vertical panel the full height of the vitrine. This was not acceptable to the designer, nor to the exhibition authorities. The display had to be free-standing, visible on all sides. After installation of about 25 Kg of gel conditioned to produce 55% R.H., readings were taken with an electronic hygrometer probe pre-installed at the tray level. It was found that the probe read consistently lower than actual, and in any case because of R.H. gradients in the interior there were lower levels in the vicinity of the Harp. It was doubtful that at any time the Harp was kept at the required level of 55% R.H. The probe was abandoned and a dial-type indicator was used (calibrated beforehand with an Assmann psychrometer).

The third experience concerns the establishment of a very dry case climate for a Benin bronze sculpture in the African Gallery of the Montreal Museum of Fine Arts. Here a compact glass case was used with the support platform concealing the silica gel within. The platform was of porous construction so that there would be reasonable transfer of humidity to the space above. The gel was prepared dry (an indicating type was used with cobalt salt indicator showing blue when dry). About 15 Kg of silica gel was placed in the concealed platform. After 6 months observation the R.H. level in the case was of the order of 10%. There was initially indication of possible Bronze Disease in some very small patch-like areas. In the meantime, until remedial action can take place, the Bronze is very stable. Photographs taken of the affected areas show no change in the interval of enclosure in the case. Finally some experiments were carried out to determine the reading error of the R.H. on the paper-card cobalt salt R.H. indicators. In controlled tests in micro-environments, controlled by saturated salt solutions, a technique of reading can be developed accurate to within about 2-3 % on each side of the psychrometric true value. There is of course a very attractive feature in probes. Further development work must be done with these to make them more reliable, i.e. free of drift, independent of

81/18/8-4

contamination factors, and sufficiently unobtrusive in the case display. Until such improvements are realized it is more prudent for simple devices, such as humidity cards, be used for monitoring the case R.H.

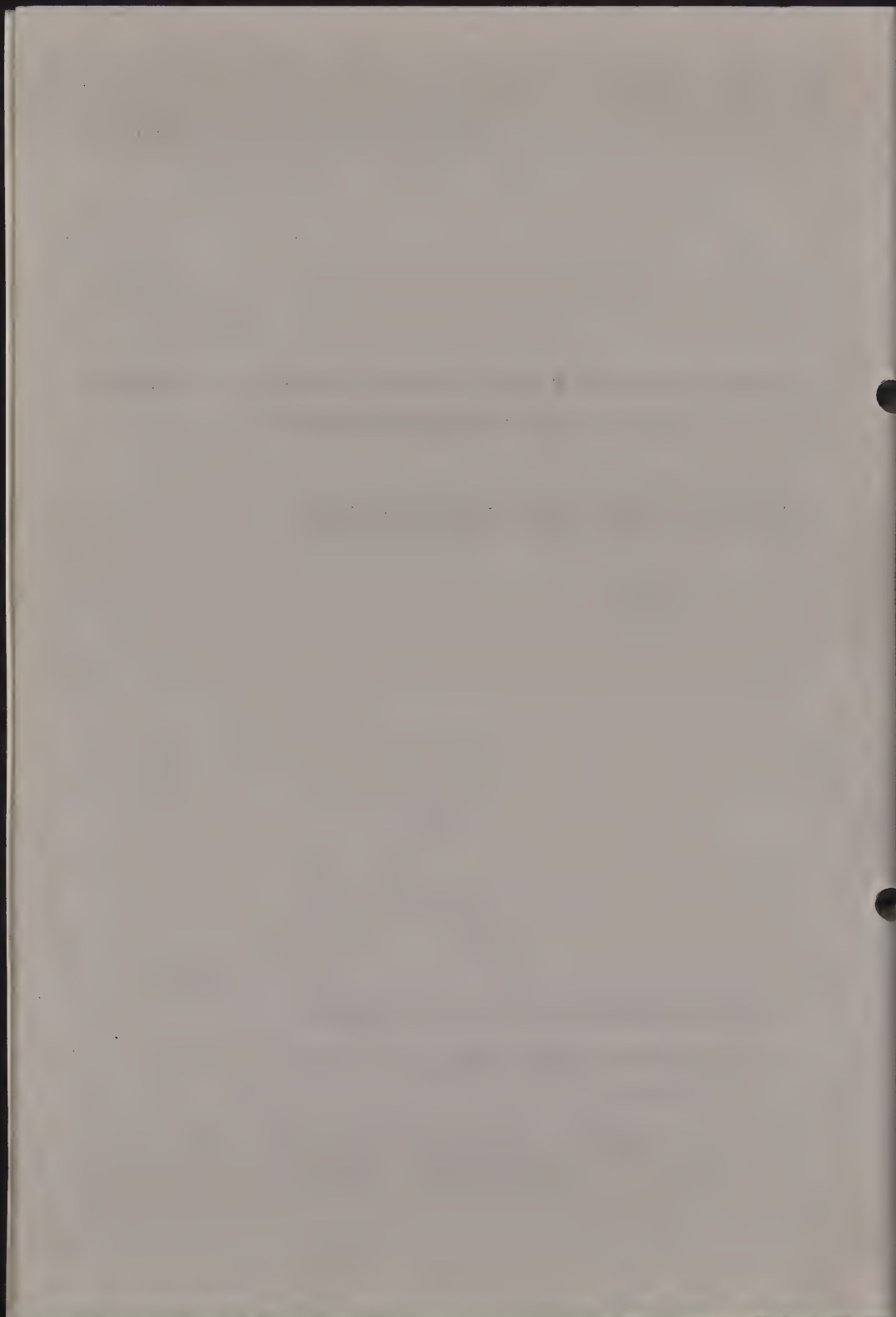
81/18/9

CLEAR WEATHER PRECIPITATION INSIDE A MUSEUM:
A CASE STUDY IN MICROMETEOROLOGY

Tim Padfield and David Erhardt

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting



CLEAR WEATHER PRECIPITATION INSIDE A MUSEUM: A CASE STUDY
IN MICROMETEOROLOGY

Tim Padfield and David Erhardt

Conservation Analytical Laboratory
Smithsonian Institution
Washington, DC 20560
USA

Solutions of wood fireproofing salts drip from its roof into the Arts and Industries Building of the Smithsonian Institution. This has occurred on clear sunny days in the spring and early summer since the present roof was installed three years ago. This paper describes how the construction of the roof, the materials used and the local environmental conditions have caused this unusual phenomenon. We describe the techniques used to measure the environmental conditions within discrete layers of the roof. The measurements have not yet followed the roof through its annual cycle; but we propose a mechanism based on data gathered so far.

The Arts and Industries building of the Smithsonian Institution was finished in 1881. It was built as a temporary shelter for some of the pieces from the Philadelphia Bicentennial Exhibition. It continued in temporary use sufficiently long to be put on the National Register of Historic Buildings and its future seemed secure - until it was re-roofed about three years ago. The new roof displays the peculiar property of dropping rain into the halls below during fine summer weather above.

Our investigation of this bizarre phenomenon is not yet complete, but our ideas and the experimental techniques we have developed may interest the reader and we hope to have learned much more by the time of this Ottawa meeting of ICOM Conservation Committee. The problem was first reported verbally by R. M. Organ at the 1980 Vienna Congress of I.I.C. under the title: "Rain within, no rain without: how a roof reversed its role."

The rain is in fact a concentrated solution of fireproofing salts leached out of the roof timber. This is a mixture of boric acid, ammonium sulphate and ammonium dihydrogen phosphate. Evidently some condensation is occurring within the roof but the timing mechanism for the escape of the liquid into the museum halls is a puzzle.

The roof is sketched in fig 1. The particular part that gives trouble, the "transitional roof," is marked by hatching. The details of construction are shown in fig 2.

The new roof was designed to match the old in appearance both inside and out and in thickness. It had to be better insulated and fire resistant. It had to be installed without risk to the exhibits below, many of which were massive machines, difficult to remove and store. These various demands forced an unorthodox design.

The roof consists of a set of prefabricated plywood boxes stuffed with insulation. Each box just spans two of the original roof girders. The top layers of tarred paper and lead clad copper sheet were applied after the boxes had been bolted to the girders. This method of construction means that there are gaps in both the vapour barrier and in insulation between the boxes. The copper roof is not airtight, so air can flow through the roof. The boxes will also breathe through the daily cycle of thermal expansion and contraction of the air within. All parts of the roof are therefore exposed to flowing air and will add or subtract moisture according to the local RH, which in turn is defined by the local temperature, the moisture content of the plywood laminae and the rate of diffusion of water through the plywood.

At times the roof becomes so wet that salt solution formed at the wood surfaces migrates upwards through the tar paper layer. The lead cladding on the under surface of the copper roof sheets is badly corroded with a patina of lead borate hydrate, basic lead phosphate and lead carbonate. The zinc coated steel ceiling panels are also corroded and the iron girders are partly covered with an efflorescence, mainly of fireproofing salts. Ammonium dihydrogen phosphate is a good nutrient and so fungal hyphae twine around its crystals on the wood surface.

In winter air always moves outwards through the roof. This is the 'Stack Effect'. The warm, relatively moist air in the building is lighter than an equal column of cold outside air. This warm air will float upwards and escape through the porous roof to be replaced by a flow of cold air through the door. In summer the process reverses. The rate of percolation of air depends on the temperature difference.

Moisture will condense on the roof timber above 80% RH at all normal temperatures. This is a consequence of the hygroscopicity of ammonium sulphate which impregnates the wood. Above about 80% RH this substance absorbs water from the air to form a saturated solution. Even below this RH the salt enhances the moisture absorption of the wood, making it a powerful buffer for atmospheric moisture. One might suppose that condensation would occur first on the salt impregnated wood - but this is not always so. On a cold winter night the outer metal skin becomes so much colder than the top of the plywood that air reaches 100% RH at the inner metal surface before it reaches 80% RH at the wood surface.

Condensed moisture can migrate slowly through the plywood. Moisture taken up from the box cavity by the upper plywood migrates to the upper surface

and evaporates to re-condense on the metal skin, often as ice. When the skin warms up the ice melts, the water clings to the metal, flows down the slope and escapes to the outside of the roof through the folded-over horizontal joints. So the roof partially dries itself through a condensation process!

In summer the moisture accumulated in the upper plywood returns to the interior. Air enters the roof and warms above ambient as it passes through the sun heated roof. Its RH drops so the plywood releases moisture to the warm air. Warm moist air is also forced out of the box sections as the top plywood heats up. Remember that moist wood tries to maintain a constant RH in the surrounding air regardless of the temperature. This warm moist air cools as it passes between the box sections to the cool interior of the building. Its RH increases but there is only a small area of wood in its path to buffer the increasing RH. Eventually condensation occurs on the tops of the metal girders which are cooled by the well stirred air inside the building and have become coated with an efflorescence of fireproofing salts.

This multitude of interacting processes makes difficult the accurate diagnosis which must precede any remedial work. We have therefore been forced to make measurements! Our experimental techniques may be of some interest because the measurement of relative humidity in confined spaces has received much less attention than measurements in free flowing air.

There are several physical processes that have been harnessed to measure relative humidity. In a confined space with little exchange of air and good heat insulation some of these measurement processes will themselves affect the RH of the air they are sampling. In a remote, rather inaccessible place the list of suitable RH sensitive processes is further restricted by the need for automatic data collection and long cable runs. We chose one of the group of RH sensors which use the change in electrical resistance of a hygroscopic electrolyte. One suitable and long established sensor is the type PCRCII made by the Phys-Chemical Research Corp. 36 West 20th Street, New York, NY 10011.

The sensor is a polystyrene wafer with a sulfonated surface layer which increases in conductivity as the RH increases because the adsorbed water film allows the sulfonic acid groups to ionize. This surface has two electrodes printed on in an interlocking maze. The amount of water involved in the equilibrium is minute and the sensor does not appreciably alter the RH of even a small volume of still air.

The flatness of our chosen sensor is a great advantage for studying laminar structures but the sensitive surfaces must be held away from other materials, drips and floods. We rolled a sheet of stiff polyester film into a cylinder and stapled it. Another roll of polyester was pushed into this cylinder to prevent the metal staple from short circuiting the sensor. The springy composite cylinder was then squashed into an oval while the sensor was inserted (see fig. 3 for details of sensor construction).

There are calibration problems with these variable resistance sensors

and also some complexities in processing the observed resistance of the device into RH. The resistance must be measured by an alternating current circuit - even momentary d.c. will destroy the calibration. Most electronic data recorders insist on a d.c. voltage source. The simple conversion circuit shown in fig.4 uses a stabilized 1.4 v a.c. supply across the sensor and a fixed resistor in series. The voltage across the fixed resistor is rectified by the ac/dc converter and is then sent to the data recorder. The 60 Hz signal can be transmitted over a few hundred feet of cable without appreciable losses.

This sensor is temperature sensitive and the temperature coefficient of the RH itself varies with both temperature and relative humidity. There is a small amount of hysteresis. Nevertheless this sensor, or similar devices which use the resistance change of absorbent surface films with RH, seems the best for this sort of job.

The temperature sensors are copper-constantan thermocouples. They are made of 0.010 inch dia. wire insulated by a bake-on silicone coating and further protected from the corrosive salt solution by a polyethylene sleeving filled with magnesium oxide.

Another vital measurement is the direction of air flow through the roof. We detect this flow in a tube passing through the roof. A thermocouple within the tube indicates either the inside or the outside temperature depending on the direction of the movement of air. All these sensing devices are sketched in fig. 3 together with a drawing of our outside weather station.

The way in which the sensors are disposed through the roof is drawn in fig. 5. Our tentative interpretation of the condensation processes is summarized in fig. 6. We hope to be able to refine this in our final report so there is no detailed description!

Acknowledgements: We are grateful for the help and interest shown by Robert Ridgley, who designed the roof.

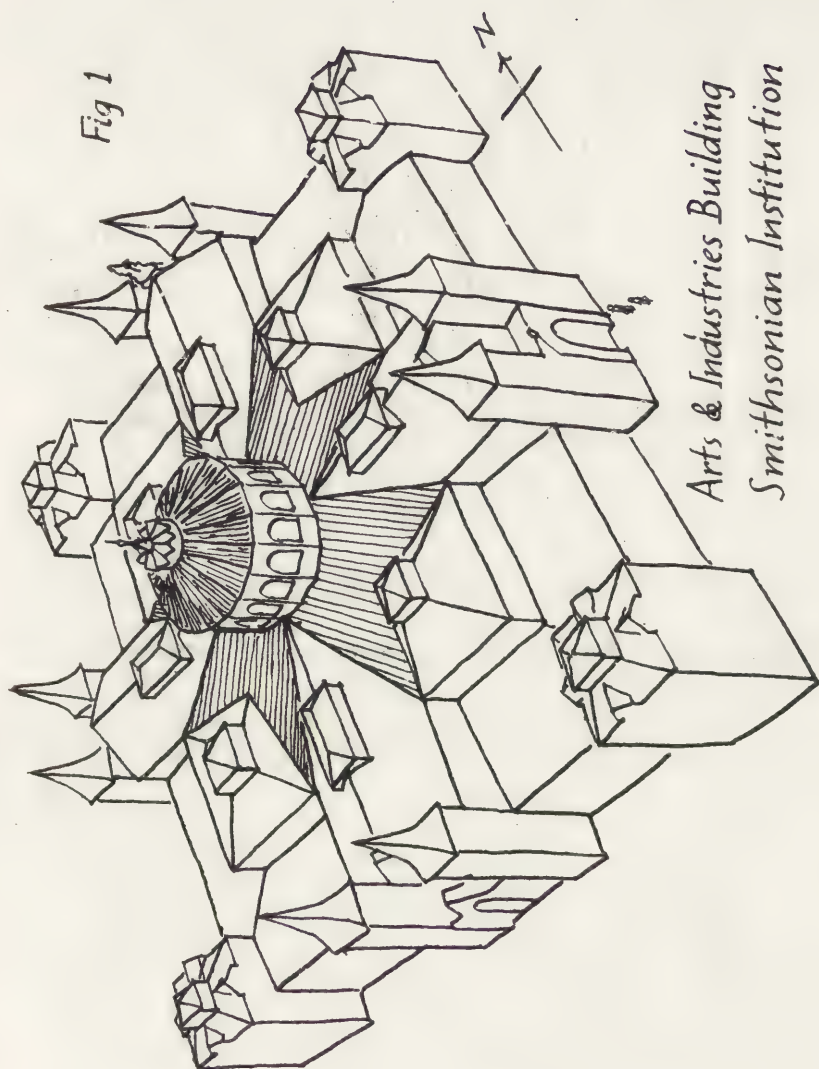
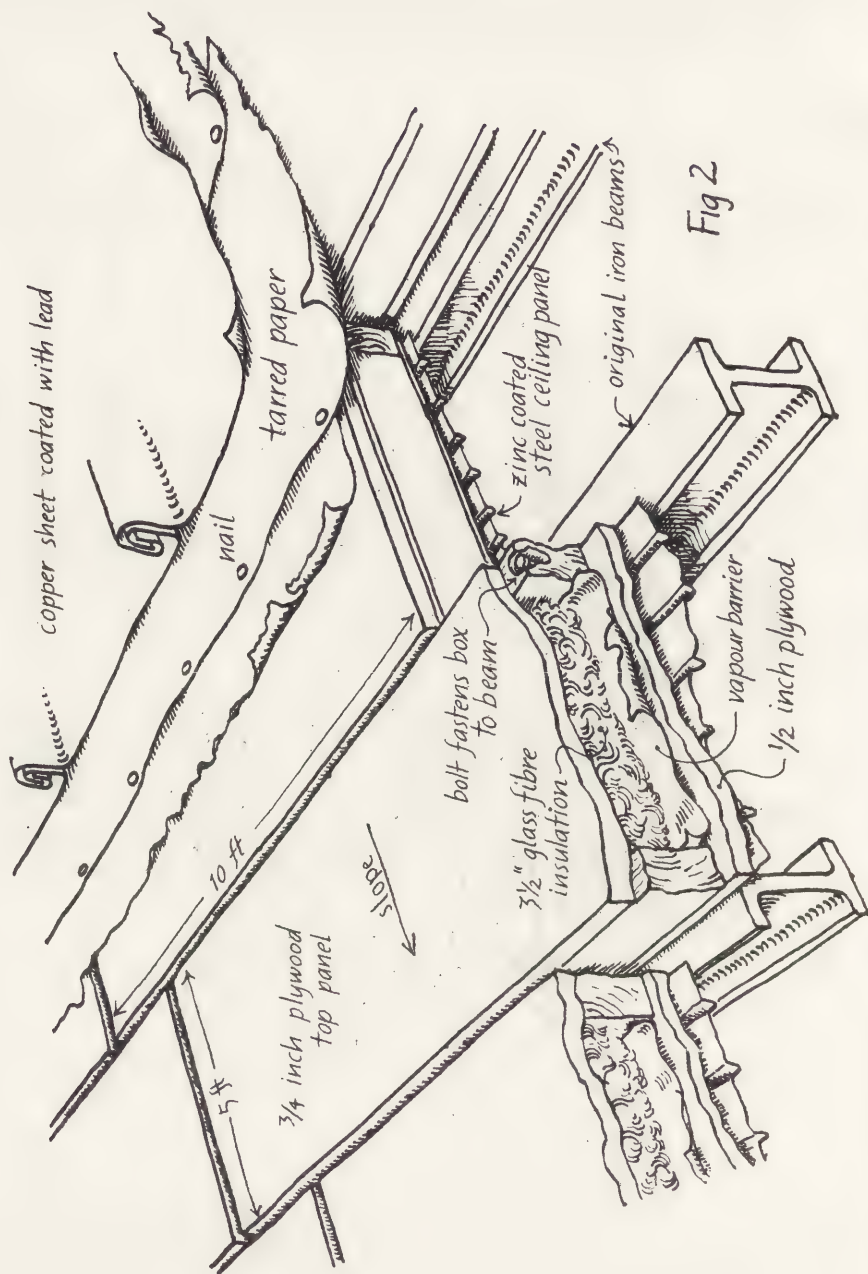


Fig 1

Arts & Industries Building
Smithsonian Institution



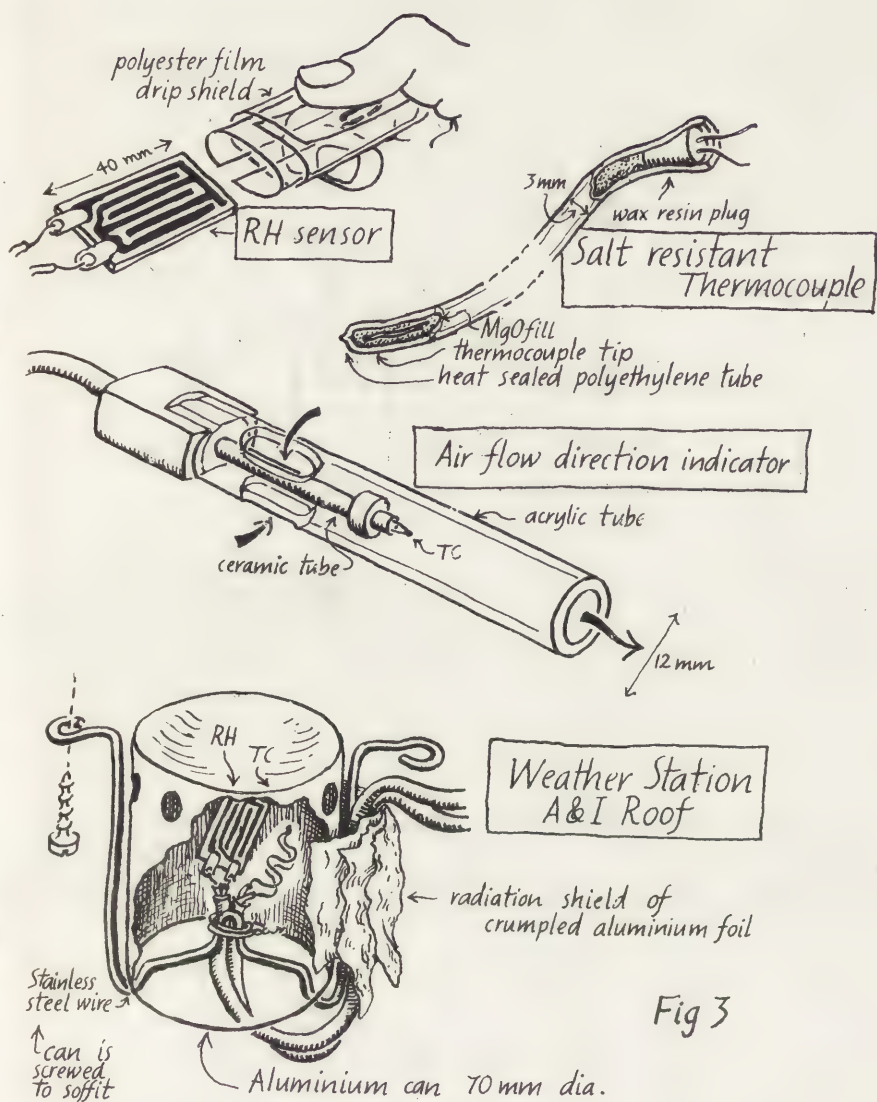
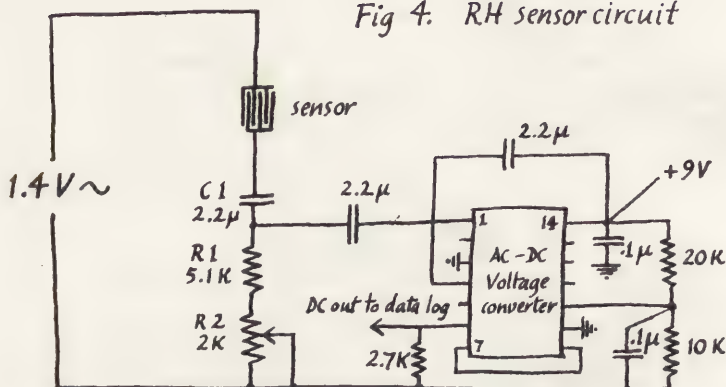


Fig 4. RH sensor circuit



A stable ac voltage of about 1.4V is applied across the resistor chain: Sensor, R1 and R2 in parallel with the 16K internal resistance of the ac to dc converter which is an Analogue Devices type AD 536 AJD. The ac voltage developed at the junction of C1 and R1 varies with the resistance of the sensor. This voltage passes to the ac to dc converter. The dc output goes to the data logger.

Notes on the circuit:

R1 and R2 plus the internal resistance of the converter are chosen to prevent the sensor passing more than 0.7 mA at 100%RH. C1 prevents dc from hitting the sensor - it would be destroyed. All other components bias the various inputs to the converter according to the manufacturer's recommendations.

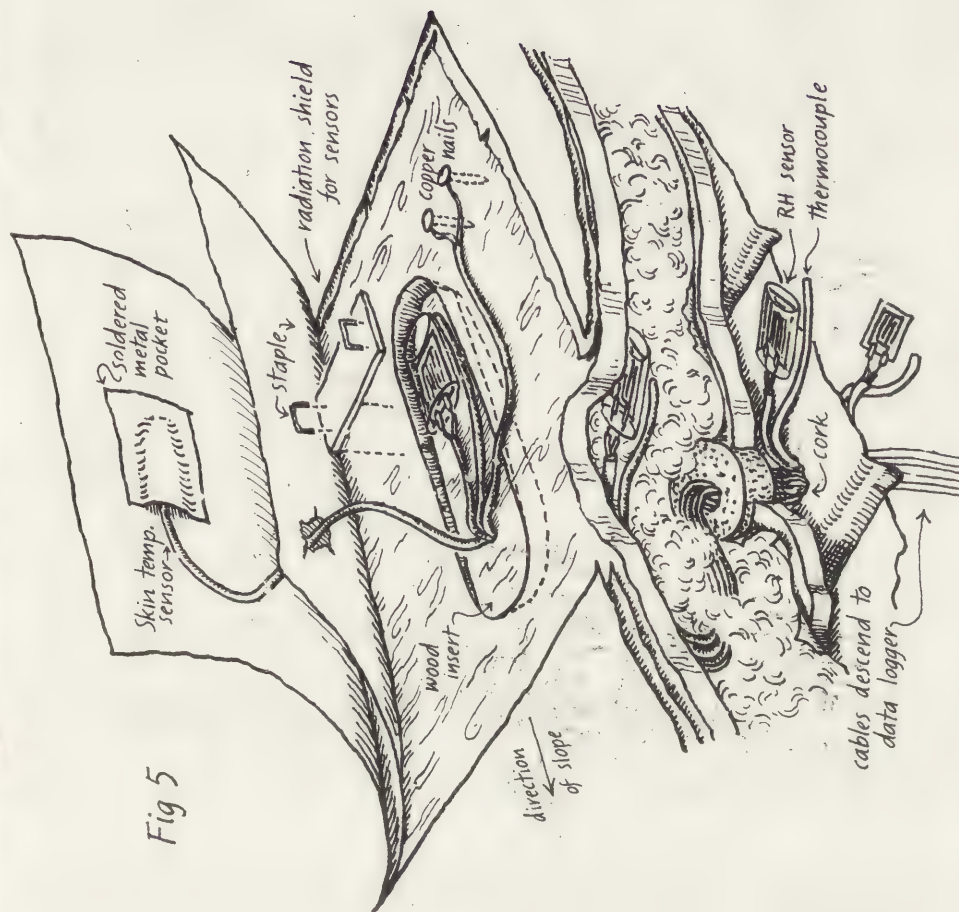
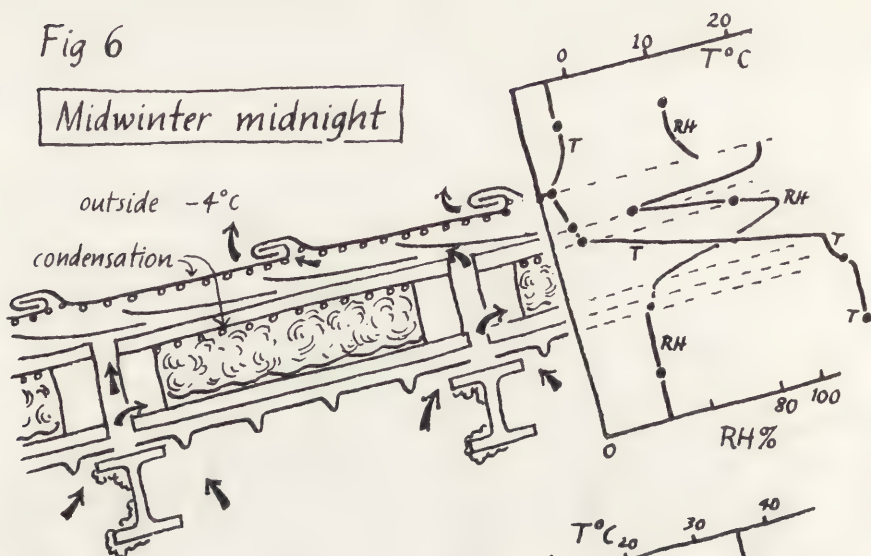
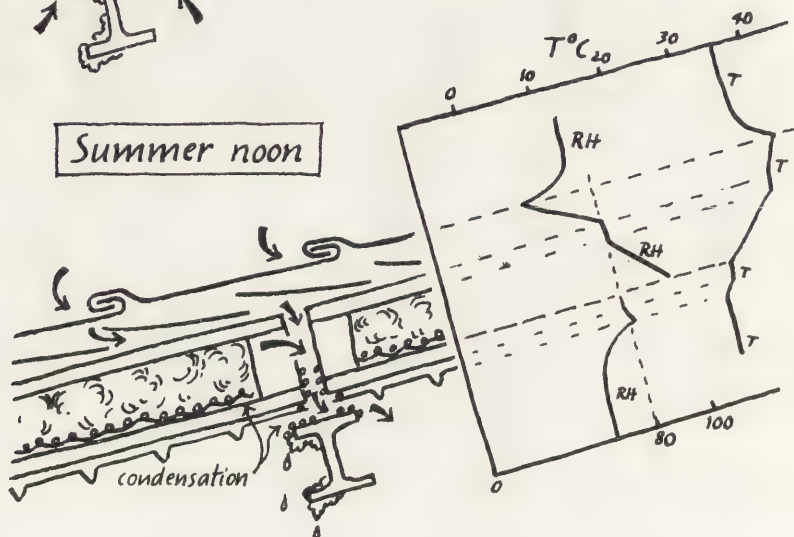


Fig 6

Midwinter midnight



Summer noon



In winter air passes through the roof from the inside. Condensation occurs on the upper inner surface of the box and on the lower surface of the roof skin. These are the coldest surfaces of the two main air spaces in the structure.

In summer air enters the roof from outside. The upper plywood, moistened by winter condensation, buffers the air above it to 80% RH at a temperature raised above ambient by solar radiation falling on the grey roof. This air stream descends between the boxes and is augmented by warm moist air expanding outwards from the box interior. The air cools and water condenses out, dissolves the efflorescence and drips to the floor.

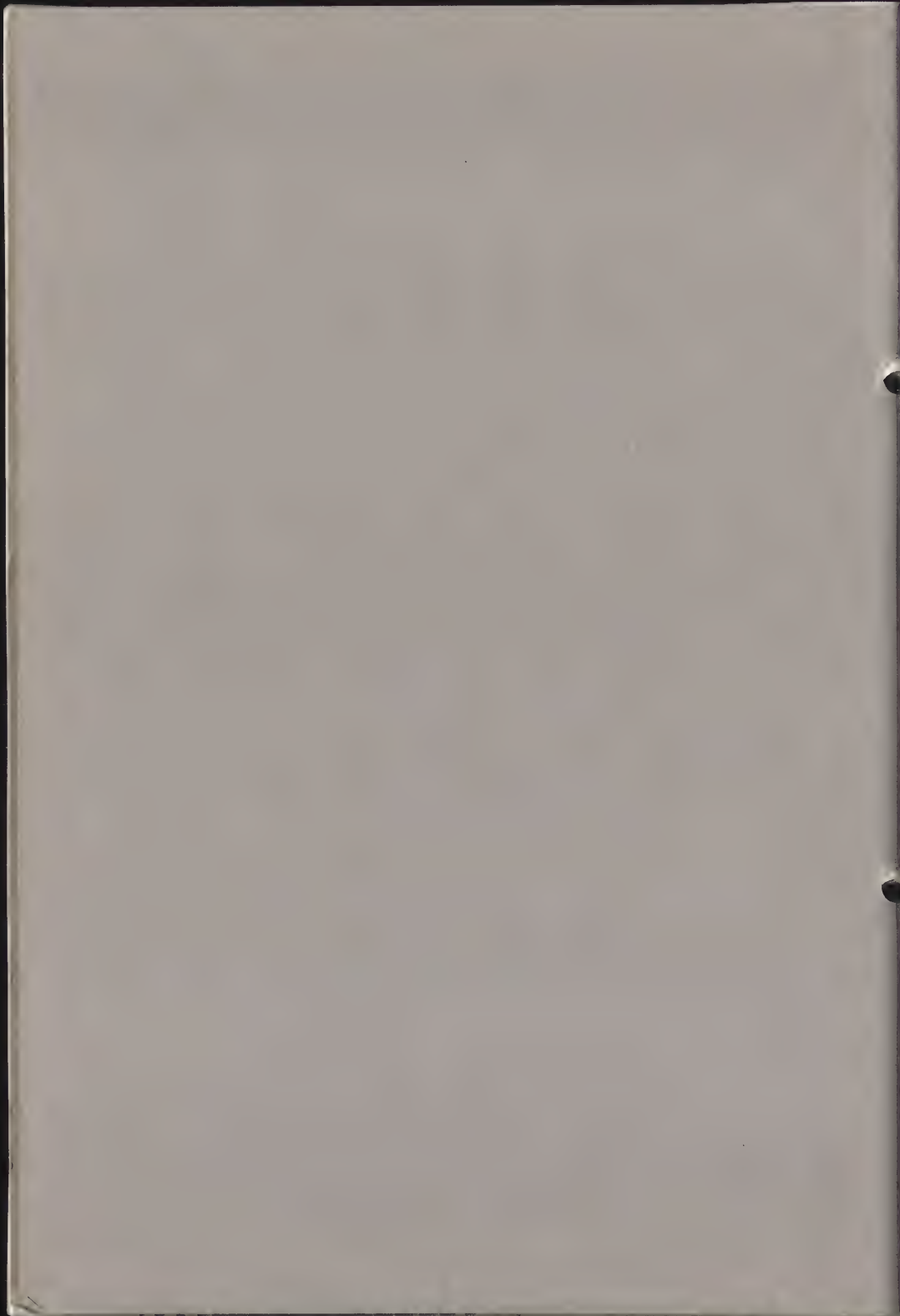
81/18/10

MICROCLIMATE FOR MURALS

Cvetko Kadijsky

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting



MICROCLIMATE FOR MURALS

Cvetko Kadijsky

NIPK

44 Dondukov str.

Sofia

Bulgaria

The paper describes the general lines of the results obtained from several year of work, related to controlling the climate in the monuments, containing murals and offers a general presentation about the character, scope and results from the work performed. It describes the recommendations for the inside parameters as well as for adopting of outside winter temperature higher than the standart one. Tentative data have also been determined about the averige number of visitors and the heat load resulting from illumination. As far as to the vapious systems of heating and ventilatinn with the view to the application in the monuments, particular attention is to be paid to the floor heating, to air-heating and coditioning, with particular reference to autonome units. On the bases of the analysis and the conclusions drawn from our work, a set of recommendations for design work is prepared. Based on those Recommendations, designs and specifications have been prepared for sets of equipment, used in main - taining the climate in a number of monuments in Bulgaria.

Strictly speaking, under the term of microclimate in certain places we mean the condition of the air characterized by certain values of the temperature, the relative humidity, dust content in the air and noise level. For several years now we have been engaged in research and practical work related to controlling the microclimate in the monuments of religious architecture containing murals.

It is not possible to examine, in one paper, all aspects of the comprehensive treatment of the problem carried out by us. That is why we find it expedient to offer here a general presentation about the character, scope and results from the work performed. We are prepared to provide further information to all members of the working group "Climate and Lighting Control" who are interested in details from our experience.

Along general lines, the results obtained from several years of work can be summarised as follows:

An analysis has been made of the factors of the microclimate which lead to the destruction of the work of art in these monuments. Substantiation has been adduced for accepting humidity and temperature as criteria for evaluating the microclimate from the point of view of preserving the monuments. A method for measuring the parameters of the microclimate in such monuments has been worked out, and recommendations have been made relative to the measuring apparatuses and to the processing and presentation of the results. Measurements have been made in numerous monuments of church architecture on the bases of the methods designed. It should be pointed out that obtaining data about the variation of the parameters involved is not an end in itself: an analysis of these data enables us to determine the limits and the rates of change in the temperature and, primarily, of the humidity, the

conditions for the formation of condense moisture, the conditions determining the increase or the abatement of evaporation through walls as a result of capillary humidity, the temperature and humidity gradients along the vertical, the influence of the secondary disturbing factors (illumination and visitors). In addition, the results from these measurements provide information about the limits of temperature variations on surfaces on which the murals are painted, about the danger of freezing to the plaster and of the measurement of the moisture on it. Combined with the measurement of the moisture at the surface layer of the wall and in depth, these measurements provide information about the nature of the humidity (condense, capillary, or infiltration), and about the effect of increased capillarity.

The optimum parameters of the microclimate which must be maintained, with a view to the specific requirements for preserving the monuments, have been established as well. According to the results of our research, the temperature should not drop below $6-8^{\circ}\text{C}$ during the winter season. When the study of the microclimate indicates that in view of increased number of visitors or of the special requirements on the illumination it is necessary to control the inside air temperature in summer as well, the later should not exceed 20 or 25°C in the general case.

Substantiation has been offered for the pattern of transition from winter to summer conditions, and vice versa, both with a view to the maintenance of optimum conditions for preserving the murals and for avoiding the temperature variation. Ensuing from studies performed in specialised research institutes into the stability of building materials, we accept $\pm 1.5^{\circ}/\text{hour}$ as the maximum admissible rate of temperature change.

It may be assumed, with a first approximation, that the universal optimum value of RH is 50-55 per cent. In all cases we recommend that these tentative values be checked for the concrete structural and physical characteristics of the building and for the climatic conditions of the climatic zone in which the monument is situated. The basic criterion of adopting a certain parameter is not to allow any freezing of the mural layer or the condensation of water on it.

As a matter of principle, the parameters of the air in these monuments must be in accord with the general requirement for murals, while the requirements for convenience to visitors or to the people working within the monuments shall be observed only if they are not contradictory to the former requirements. Moreover, decisive are

not so much the values of the parameter as is the rate of their variation in time.

A method has been designed for determining the heat losses and gains in such monuments, as well as diagrams for rendering practical work easier. Substantiation has been offered for adopting, for conditions prevalent in Bulgaria, of outside winter temperatures by 4° higher than the standard calculation temperature, and corroboration has been obtained for that by empirical checks in concrete monuments. This modification in the calculation temperature will, in our opinion, lead to a certain economy in capital investment and in energy. Tentative data have also been obtained about the average number of visitors normally in the monument and the heat load resulting from illumination. The exact number, type and power of the illuminants are determined by the respective artist or architect. For the purpose of preliminary calculation we suggest that the climate-control engineer shall have the following data under consideration (illuminant power reduced to 1 sq.m. of floor area):

- incandescent filament lamps 5 - 20 W/m²
- luminiscent lamps 2 - 5 W/m²

It is necessary to take account of the thermal accumulation by the surrounding structures with respect to heat that has penetrated from illumination or solar radiation and that is why we have worked out tables and nomograms for prompt and convenient operation.

An analysis has been made of the thermoengineering measures applied in improving the temperature-moisture conditions in the monuments of culture, with discussions of their favourable and unfavourable aspects. Arguments have been adduced for using systems of heating, ventilation, and air-conditioning as the sole means of controlling condense moisture and of eliminating the influence of the secondary disturbing factors (illumination and visits).

Climate curves have been plotted for the different premises within these monuments. Frequency and summary diagrams have been worked out on their basis about the applicability of ventilation to the purposes of maintaining the microclimate. It was proved that the operation of natural ventilation is uncertain and ineffective. Mechanical ventilation can be used successfully for drying primarily in winter, when the air possesses a relatively high drying capacity (even with relative humidity of over 90 per cent). Of course, it is necessary to compensate for the cooling effect of the cold air used in ventilating the particular premise, so that the temperature shall not drop below the admissible values. Besides that, we offer proof to the possibility of a considerable reduc-

tion in the amount of fresh air used for ventilation or for air-conditioning (not more than $7-10\text{m}^3/\text{hour.man}$ instead of the usual $20-30\text{ m}^3/\text{hour.man}$).

The analysis covers various systems of heating, ventilation, and air-conditioning with a view to their application in the monuments for the maintenance of the parameters required for the preservation of the works of art. Particular attention has been paid to floor heating, to air-heating and air-conditioning (with particular reference to central and autonomic systems and to systems for dehumidification). Diagrams have been worked out for calculation-type floor heating installations which are very promising both from a technological point of view and on account of the economy of energy involved.

We consider the autonomous units as the most suitable items of equipment for air-conditioning. The use of sprinkler chambers is not to be recommended, and it is preferable to use steam humidifiers. The use of a refrigeration machine is most expedient for cooling (and for drying), unless it is a case of small air-conditioning installations in places with regular water-supply, in which instance it is possible to adopt a system of direct water-cooled condensers with running water. In our opinion, solid absorbents may be used only under emergency conditions. We likewise recommend restraint in the use of liquid absorbent.

On the basis of the analysis and of the conclusions drawn from our work, we have prepared a set of recommendations (Indications for design work) as to the principles of creating the optimum microclimate in the monuments of church architecture. Based on these Recommendations, designs and specifications have been prepared for sets of equipment used in maintaining the microclimate in a number of monuments (Boyana Church, the Crypt of the Alexander Nevsky Memorial Church in Sofia and the church itself, the Saint George Church in Sofia, the Roman Tomb in Silistra, the Saint Petka Church in Sofia, and a number of other monuments), some of which are already in operation, while others are in the process of construction.

81/18/11

CREATION OF THE REQUIRED TEMPERATURE-
HUMIDITY CONDITIONS IN MONUMENTS OF CULT
ARCHITECTURE-MUSEUMS, BY MEANS OF HEATING,
VENTILATION AND AIRCONDITIONING

V. Boiko, R.A.Devina, I.B. Illarionova
and Ts. Kadiski

ICOM Committee for Conservation
6th Triennial Meeting
Ottawa 1981

Working Group: Control of Climate and
Lighting

CREATION OF THE REQUIRED TEMPERATURE-HUMIDITY CONDITIONS
IN MONUMENTS OF CULT ARCHITECTURE-MUSEUMS, BY MEANS OF
HEATING, VENTILATION AND AIRCONDITIONING

V. Boiko, R.A.Devina, I.B.Illarionova and Ts. Kadiski

WCNILKR

10 Khrestyanskaya pl.

109172 Moscow

USSR

Works of art which are placed in monuments of cult architecture, particularly mural paintings and iconostases, are constantly under the action of unfavourable microclimate. This action results in chemical and physical changes in the materials, which cause irreparable destruction of the exhibits and monuments themselves. Changes in the conditions of temperature and humidity are one of the main causes of this destruction.

The difficulty of creating the required climatic conditions in the building which is a monument of cult architecture is explained by several causes among which considerable importance is attributed to architectural and structural features of the particular kind of buildings. To determine and to substantiate the conditions of temperature and humidity required for their conservation, and to create them with the aid of heating, ventilation and air-conditioning, it is necessary to make comprehensive examination of the monument and to find out the degree to which all the factors influence the temperature - humidity conditions in the whole air space of the building.

To achieve this purpose, early in the year 1976 the USSR Research Institute of Restoration together with the National Institute of Monuments of culture in

the People's Republic of Bulgaria developed a Program of joint researches on the subject of "Creation of the optimal temperature-humidity conditions in monuments of cult architecture-museums - by means of heating, ventilation and air-conditioning."

The Program describes: the subject of research, the problems involved, and the final result.

The subjects of our research are monuments of cult architecture (cathedrals, churches) having mural paintings and iconostases. Most monuments have no technical devices for maintaining the necessary conditions. Constructive solutions concerning systems of heating, ventilation and air-conditioning, which exist in some monuments, do not ensure the required microclimate.

The difficulty encountered in the problem under consideration is that buildings-monuments differ from one another in their architecture and lay-out.

These features do not enable one to apply to these buildings construction standards and rules developed for living quarters, public buildings and industrial enterprises. The choice of rated temperature of the outer air according to the rules chosen for modern buildings may also result in erroneous decisions.

A methodological structure of investigations comprising the most progressive technique of laboratory research - the method of physical simulation - has been developed to solve the problem that was set before the researchers.

Taking into account these considerations, the researchers undertook the following tasks and solved them:

1. The development of methods concerning the investigation of temperature-humidity regime under natural conditions, taking into consideration the characteristic features of monuments in the USSR and PRB.

2. The development of methods applied to in the examination of heat engineering and aerodynamic processes on models.

3. Complex studies in factors determining the microclimate in monuments.

These tasks included:

3.1. Studies on the influence of outer meteorological conditions, on the inner regime in monuments. Provision was made for studies in nature as well as for model aerodynamic tests for the influence of pressure, wind velocity, temperature and the relative humidity of air.

3.2. Studies of heat-engineering properties of building barriers (characteristics of air penetration, designing realization of space with different plans and the relations between the outer barriers fitted with glass and those that are not fitted with glass).

3.3. Studies on the formation of temperature-humidity fields, air streams inside buildings when the influence of outer factors and the presence of visitors are taken into consideration.

4. One of the important problems is the method of calculating heat losses and heat gain for such specific buildings as monuments of cult architecture. These methods were compared and the technique that is required for use in such monuments was determined.

5. Development of heating, ventilation and air conditioning systems, which should be the most rational for monuments having complicated three-dimensional structures.

6. Recording the typology of monuments located in the USSR territory in view of organization of their inner space; this record is necessary when one or another form of air distribution in ventilating and air conditioning is to be chosen.

The data obtained in the first stage of this research were stated in the paper read at the conference of the Conservation Committee, which took place in Zagreb in 1976; they were published also in Zagreb, and contained the main material concerning the methods used for the temperature-humidity regime in natural conditions, with due regard for peculiarities of monuments in USSR and PRB.

At the present time studies made according to the above-mentioned program have been completed.

In this paper we shall dwell on the description of the data, obtained in the following parts of our work:

1. The investigation of aerodynamic properties of buildings that are monuments of cult architecture.
2. The investigation of air-distribution schemes in the above mentioned buildings.
3. The principles of determining temperature and relative humidity parameters for designing climatization systems in monuments of cult architecture.

1. The investigation of aerodynamic properties of buildings

Formation of temperature fields and airstreams inside the monument takes place due to the infiltration of outer air or to the exfiltration of air from the building. Natural airexchange in buildings is due to the fact that in some window openings and doorways pressure inside the building is lower than the outer atmospheric pressure, while in others it is higher than the outer pressure.

Difference in pressures may take place under the action of gravitational forces, of wind or under their joint action. One may neglect the action of gravitational forces because they are slight. The researchers studied only the influence of wind action. To estimate the value of wind pressure they built a model that was

geometrically similar to the wide-spread type of cult buildings - four-pillar churches with five cupolas shaped like the cross. The scale of the model m 1:100 was chosen in accordance with the condition of automodeling. To determine the numerical value of wind pressure strong air current was sent through the model of the building by means of aerodynamic stand. Aerodynamic tests on the model were made when the angle of wind attack towards the axis of the building was 0° , $+90^\circ$, $+45^\circ$, -45° , -90° . The locations of aerodynamic openings were marked on the surfaces of the model by depressions ($d - 4 \text{ mm}$, $h - 5 \text{ mm}$), pressure in them was measured with a needle-shaped pneumatic tube of specific design, connected with a manometer.

Calculation of aerodynamic coefficients was made in accordance with the formula:

$$K = \frac{\Delta p}{\rho \cdot \frac{v^2}{2}}$$

where $\frac{\Delta p}{\rho}$ is excessive pressure on the surface of the model kgp/m^2 ; ρ is air density, kg/m^3 ; v^2 is the velocity of air in the working opening of the aerodynamic stand, m/s .

The investigations showed that four-pillar churches with five cross-shaped domes possess favourable aerodynamic characteristics. As the cylindrical domes are arranged symmetrically, the airstreams are superimposed behind the domes, and this produces negative pressure in the windows of the domes located in the zone of aerodynamic shadow. Thus, irrespective of the direction of wind these window openings can be used as openings inaccessible to the wind and contributing to ventilation by extraction. The quantity of window openings that intensify exfiltration is twice as large as the quantity of openings that intensify infiltration. If pressure head whose air space is small is created inside the building, then, by using forced ventilation

When air conditioning is introduced, it becomes possible to eliminate air infiltration through incompact parts in window openings and doorways. This circumstance should be taken into account in estimating the air-thermal regime of the building, which makes the stabilization of inner microclimate possible.

2. Investigation of air distribution schemes

Analysis of characteristic features possessed by monuments of cult architecture (architectural and constructive lay out, air exchange, heat radiating sources in the lower zone, the aesthetic value of the interior) enables us to state that proper organization of air exchange is the most rational means of creating microclimate. Air exchange in buildings is caused by transfer of certain (rated) volumes of air from inlet openings to exhaust ventholes. Three schemes of air distribution were to be investigated. The investigation was conducted on the model of a building whose inner space was geometrically similar to a four-pillar church with five cross-shaped domes. As a result of calculations made with the computer the researchers carried out a detailed analysis of conditions which ensure the similarity of physical values and airstreams moving in the volumetric model of the building under study.

The research data show that for buildings whose air space equals 150 m^3 and whose height is about 10 m, while their iconostasis does not occupy the full length of the church, it is advisable to make use of an air-heating curtain which consists of an air-entrapping device, calorifers, an irrigator and an air-distributing box. The aggregate channel is supplied with two air-distributing nozzles; one of them lets the air out at an angle to the tambour ($1/3/\text{t.v.}$), the other lets the air out perpendicularly to the plane of the gate into

the church. The double-flow air curtain ensures the required thermal support in the tambour. The second jet produces additional thermal protection and thus eliminates the penetration of the outer cool air into the building. The action of the second flow ensures the influx of heated air for producing the required microclimate in the monument. Using the proposed design of the air-heat curtain with irrigation in a building with a single air-space does exclude an installation of heating systems, laying of air channels and other kinds of constructing which badly disfort the initial interior of the monument. The air is let out of the building from two zones: through devices in the domes and by removal of the recirculated air through openings in the floor. For cult monuments with a single air space of up to 3000 m^3 and up to 15 m height it is advisable to send air to the middle zone by airdistributors with the stream twister. The application of these airdistributors makes it possible to distribute uniformly large volumes of ventilation air in a considerable area, to ensure fast damping of speeds and excessive temperatures; it makes the distribution of temperature and air speed in the whole air space of the building more uniform.

The advantage of concentrated admission of air is the simplicity of its design. The removal of air is analogous to that mentioned above.

For buildings with many naves whose air space of 10.000 m^3 and height of 20 m is divided into many parts, as well as for buildings with the height of more than 25 m and the insufficiently developed layout, one should apply an airdistribution scheme with a double-zone air inlet - downwards and up wards, and with a double-zone air outlet from the lower zone for air recirculation, and from the upper zone for air removal.

In buildings of this kind the single-zone inlet will not produce uniform good heating of the monument. When air descends into the lower zone, then in the course of its progress upwards along the inner surfaces of outer barriers, it becomes cooler and falls down in a descending stream, ejecting peripheral streams of warm air from the main outgoing stream. Streams of the cooled air from the upper zone impede the motion of the heating stream, wash out and make it cooler, while the admission of air into two zones will ensure the required parameters in the whole air space of the building.

3. Principles of determining the temperature- and relative humidity parameters in designing climatization system in monuments of architecture

In designing climatization systems one of the key problems is the choice of temperature and relative humidity parameters. There is no unanimous opinion on this point in museum practice.

Specific requirements that need to be met concerning climatic conditions are that in the first place there should be optimal conditions for conservation of objects of art; comfort of visitors should be of minor importance.

Besides, choosing the parameters of inner air in a cathedral containing mural paintings, it is necessary to be guided by problems of their conservation too.

In choosing the climate for a monument we consider it necessary to isolate first its barriers from the action of atmospheric and ground moisture. Hence, the main requirement that is to be met in creating the proper regime for conserving mural paintings is to make impossible condensation of water vapours on the inner surfaces of the walls and roofing. In determining the inner parameters one should take into account the

temperature of inner surfaces of barrier structures so, that they could not become cooler under the action of the outer air and thus reach the temperature which would produce condensation of water vapours on them.

Thus, the determination of the parameters of the inner temperature and relative humidity should be preceded by researches carried out in the monument, which have two main parts:

1. Conducting a series of nature studies aimed at obtaining regularities governing the "life" of the monument under natural conditions, involving measuring the temperature and relative humidity in various zones of the monument's air space, as well as measuring the temperature on the inner surfaces of barrier structures.

2. Investigating the heat-protective properties of massive barrier structures, for outer thermal actions change considerably in passing through these structures.

These investigations made in two cathedrals of XVII century in the city of Yaroslavl made it possible to determine the following parameters of their inner temperature and relative humidity:

In the summer period: $t^{\circ}=18\pm 1^{\circ}\text{C}$; $L=60\pm 5\%$

In the winter period: $t^{\circ}=12\pm 15^{\circ}\text{C}$; $L=60\pm 5\%$.

These parameters should not be automatically applied to other monuments for their climatization.

We believe that further investigations of this kind, conducted by our methods in other objects and in other climatic zones, will eventually result in collecting sufficient data that will enable researchers to develop normative parameters of temperature and relative humidity for monuments of architecture with mural paintings, which contain climatization systems.



81/21/1

AVANCE D'UNE BIBLIOGRAPHIE DE CONSERVATION
ET RESTAURATION DE MATERIAUX SILICEUX

C. Saldaña de Goust

Comité pour la conservation de l'ICOM
6ème Réunion triennale
Ottawa 1981

Groupe de travail: Matériaux archéologiques
siliceux



AVANCE D'UNE BIBLIOGRAPHIE DE CONSERVATION ET RESTAURATION
DE MATERIAUX SILICEUX

C. Saldaña de Goust

Instituto de Conservación y Restauración de Obras de Arte
Avenida Reyes Católicos 6
Palacio de América
Madrid 3
Espagne

RÉSUMÉ

Présentation d'une méthode de classification systématique de bibliographie permettant la recherche soit par auteurs soit par thèmes concrets. A partir des classifications déjà présentées par ICOM et par IIC/Abstracts, nous avons étudié la possibilité de préparer une bibliographie sur les problèmes de Restauration et Conservation de matériaux siliceux (Céramique et Verre). Nous sommes arrivés à la conclusion qu'il était nécessaire d'articuler cette bibliographie autour d'un cadre rigide et détaillé, tenant compte de toutes les spécialités et sources nécessaires pour notre profession.

Cette bibliographie, donne la possibilité d'être augmentée facilement par un aussi grand nombre de fiches ou de thèmes au fur et à mesure de leur publication. En même temps, la classification numérique permet son intégration directe à un programme d'ordinateur de bas prix offrant ainsi de nombreuses voies pour le futur. Nous avons classifié actuellement plus de 300 articles et présentons ici un nombre réduit de ces fiches afin de servir d'illustration à la méthode.

Elle est donc divisée en trois parties:

- Tout d'abord une relation en ordre numérique des fiches
- Deuxième partie, divisée en sept groupes qui permet la classification thématique.
- Une dernière partie avec un index alphabétique par auteurs.

TABLE DE MATIERES

- INDEX NUMÉRIQUE
- CLASSIFICATION THEMATIQUE:
 - (F). 1.- GÉNÉRAL:
 - 11.- Références générales de Conservation.
 - 12.- Ethique, Philosophie et Théorie de la Conservation.
 - 13.- Archéologie.
 - 14.- Formation des Restaurateurs.
 - (F). 2.- TECHNIQUES DE FABRICATION:
 - 21.- Développement historique des matériaux siliceux.
 - 22.- Techniques de fabrication.
 - 23.- Thèmes particuliers.
 - (F). 3.- TECHNIQUES DE CONSERVATION:
 - 31.- Alterations.
 - 32.- Méthodes appliquées à la Conservation des matériaux siliceux.
 - 33.- Conservation "in-situ".
 - 34.- Thèmes particuliers.
 - (F). 4.- ANALYSES
 - (F). 5.- PUBLICATIONS BIBLIOGRAPHIQUES (Périodiques):
 - 51.- Général: Méthodes et Techniques de Conservation.
 - 52.- Techniques de fabrication des matériaux siliceux.
 - (F). 6.- PUBLICATIONS BIBLIOGRAPHIQUES (Non périodiques):
 - 61.- Général: Méthodes et Techniques de Conservation.
 - 62.- Techniques de fabrication des matériaux siliceux.
 - 63.- Techniques de Conservation des matériaux siliceux.
 - 64.- Archéologie.
 - 65.- Analyses.
 - (F). 7.- REVUE:
 - 71.- De Conservation.
 - 72.- Autres.
- INDEX ALPHABETIQUE PAR AUTEURS

INDEX NUMERIQUE

- (F). 0001.- ICOM - CONSERVATION COMMITTEE
 "Preprints for the triennial Meetings"
 Venecia, 1975
 Zagreb, 1978
 1/11
- (F). 0002.- PLENDERLEITH, H.J.
 "The Conservation of Antiques and Works of
 Art". 2nd. ed. Oxford University Press, Lon-
 don, 1974.
 1/11; 3/31; 3/32
- (F). 0003.- SEMINARIO REGIONAL LATINOAMERICANO DE CONSER-
 VACIÓN Y RESTAURACIÓN, Mexico, 1973
 1/11
- (F). 0004.- UNESCO
 "La préservation des biens culturels, nota-
 mmment en milieu tropical". Musées et Monuments
 XI. (Publié également en anglais et en es-
 pagnol) 1969.
 1/11; 3/31; 3/32
- (F). 0005.- UNESCO
 "Musées et recherches sur le terrain" Musées
 et Monuments XII. (Publié également en anglais
 Paris, 1970
 1/11; 1/13; 3/33
- (F). 0006.- BRANDI, Cesare
 "Teoria del Restauro" Edizioni Di Storia E
 Letteratura. Roma, 1963
 1/12
- (F). 0007.- IIC - CONSERVATION IN ARCHAEOLOGY AND THE
 APPLIED ARTS: "Preprints of the 1975 Stockholm
 Congress". London, 1975
 1/12; 1/13; 3/31; 3/32
- (F). 0008.- ATKINSON, R.J.
 "Field Archaeology" (Methuen et Co. Ltd)
 2^{ème} ed. révisée.
 1/13
- (F). 0009.- WHEELER, M
 "Archaeology from the Earth" Oxford Univer-
 sity Press. London, 1954
 1/13; 3/33
- (F). 0010.- ICCROM - UNESCO
 "Worldwide Problems in the Training of Specia-
 lists in Conservation" Working Document, Re-

commendations and Summary of an International Meeting on Training in 1976. Document: UNESCO SHC 76 Conf. 643/2 Paris, June 1976
1/14

- (F). 0011.- PHILIPPOT, P
"Ensayo de Tipología sobre la Formación de Especialistas de la Conservación" 1^{er} Serlacor Documentos de Trabajo Seminario Regional Latinoamericano de Conservación y Restauración. Mexico, 1973
1/14
- (F). 0012.- BLANC, A
"Les Techniques utilisées dans les grands liers de potiers dans l'Antiquité" Revue Archéologique de l'Est et du Centre-Est, XIV Vol. 4. p. 267, Dijon, 1963.
2/21; 2/22
- (F). 0013.- FRODL - KRAFT, Eva
"Le vitrail médiéval, technique et esthétique" Cahiers de Civilisation Médiévale X^e - XII^e S. année X n° 1 (Janvier-Mars 1967)
2/22
- (F). 0014.- SINGER, F et SINGER, Sonja S.
"Industrial Ceramics" Chapman & Hall Ltd. London, 1963
2/22
- (F). 0015.- HONEY, W.B.
"European ceramic art" from the end of the Middle Ages to about 1815. Ed. Faber and Faber Ltd. London (sans date)
2/23
- (F). 0016.- ANDRE, Jean - Michel
"Restauration de la Céramique et du Verre" Office du Livre. Fribourg. Société Française du Livre, 1976
3/32
- (F). 0017.- CORPUS VITREARUM MEDII AEVI (CVMA)
"Technical Committee, Answers to the questionnaire on the conservation of windows" 7th. Conference Florence, 2-6 october, 1970.
3/32
- (F). 0018.- JACOBI, R
"Die Konservierung alter Glasmalereien" St. Lucas, 11 (1957). pp. 186-192
3/32

- (F). 0019.- LARNEY, J
 "Restoring Ceramics" Barrie & Jenkins, Lon -
 don, 1975.
 3/32
- (F). 0020.- S. MESEGUER, José
 "La Conservación de la cerámica, método y
 técnica" Miscelania de Arqueología, XXV Ani-
 vers. Cursos Internacionales Ampurias. (1947-
 1971) Separata T.II. 1974, Barcelona. Diputa-
 ción Provincial Instituto de Prehistoria y
 Arqueología. pp. 329-337.
 3/32; 3/33
-)). 0021.- WERNER, A.E.A.
 "Problems in the conservation of glass" Ann,
 1^{er} Congrès des Journées Internationales du
 Verre. Liege, 1958, pp. 189-205
 3/32
- (F). 0022.- ANON
 "Adhesives" Mach. Des. 48, nº 26. pp. 155
 (1976) also Rubber & Plastics Research Asso-
 ciation of Great Britain Abstracts, Shawbury
 14 nº 19, Abstract 7703414L (1977)
 3/34
- (F). 0023.- BRILL, R.H.
 "The scientific investigation of ancient
 glasses" Proceedings of the Eighth Interna-
 tional Congress on glass. London, 1968. pp .
 47-68. Incipient crizzling in some early gla-
 sses, Bulletin of the American Group of the
 International Institute for Conservation of
 Historic and Artistic Works, 12 (1972)
 4
-)). 0024.- INTERNATIONAL CONFERENCE ON THE APPLICATION
 OF NUCLEAR METHODS IN THE FIELD OF WORKS OF
 ART. Rome, Venice, Mai 24, 29 (1973)
 4
- (F). 0025.- ART AND ARCHAEOLOGY TECHNICAL ABSTRACT (AATA)
 Published semi-annually at the Institute of
 Fine Arts, New York University, for the In-
 ternational Institute for Conservation of
 Historic and Artistic Works,. Ed. Office:c/o
 New York University. Conservation Center Ins-
 titute of Fine Arts. 1 East 78 th Street.
 New York, 10021. (Jusqu'a 1980)
 5/51

- (F). 0026.- BOLETIN DE LA SOCIEDAD ESPAÑOLA DE CERÁMICA
c/ Serrano, 113 (Madrid) - 6 . España.
5/52; 7/72
- (F). 0027.- VON IMHOFF, H.C.
"A Basic Bibliography of Conservation. The
Literature on Conservation and Restoration of
Art and Archaeology" Preliminary Edition,
1978. with Appendix A & B. Ref. 78/O/O, Za -
greb, 1978, ICOM
6/61
- (F). 0028.- HEDVALL, J.A.; JAGITSCH, R. et OLSON, G.
"Bibliographie Technique fabrication verre"
6/62 (sans date)
- (F). 0029.- BECKSMANN, R
"Bibliographie zur Technik und Restaurierung
von Glasmalereien" Preliminary edition. Ar-
beitsstelle Corpus Vitrearum Medii Aevi.
Stuttgart - 1972.
6/63
- (F). 0030.- CONSERVATION DIVISION NHPS. (Parks Canada
INA). "Conservation of Archaeological Cera-
mics" 1570 Liverpoolcourt Ottawa Ont. KIA OH4
6/63
- (F). 0031.- NEWTON, R.G.
"Critical Bibliography on the Study of the
deterioration and the conservation of stai -
ned windows" For the British Academy Publis-
hed by the Oxford University Press, Oxford,
1974. (semblable AATA Vol. 10. n° 2)
6/63
- (F). 0032.- ROME CENTER
"Bibliographie- Vitraux" ICCROM, 13 via S.
Michele 00153 ROME (sans date)
6/63
- (F). 0033.- GAUDEL, P
"Bibliographie der archaeologischen Konser-
vierungstechnik". Ergaenzungsband des Berli-
ner Jahrbuches fuer Vor - und Fruehgeschich-
te, Bd. 2, 1969 (2. Auflage), Berlin.
6/64
- (F). 0034.- SAYRE, E.V. et MEYERS, P
"Nuclear activation applied to materials of
art and archaeology" annotation. AATA Vol. 8
n° 4. 71.
6/65

- (F). 0035.- BOULETINO DELL 'ISTITUTO CENTRALE DEL RESTAU-
RO. Piazza S. Francesco di Paola, 9. 00184.
Rome (Italie)
7/71
- (F). 0036.- ANNALES DU LABORATOIRE DE RECHERCHE DES MU-
SÉES DE FRANCE. 10, rue de l'Abbaye, 75006 Pa-
ris (France)
7/71
- (F). 0037.- BULLETIN DE L'INSTITUT ROYAL DU PATRIMOINE
ARTISTIQUE. One Parc du Cinquantenaire BIO40
Bruxelles (Belgique)
7/71
-). 0038.- CCI
The Journal of the Canadian Conservation Ins-
titue The National Museums of Canada, 1030
innesroad. Ottawa. Canada. KIA OM8
7/71
- (F). 0039.- INFORMES Y TRABAJOS DEL INSTITUTO DE CONSERVA-
CION Y RESTAURACION DE OBRAS DE ARTE. Avda Re-
yes Católicos, 6 Madrid - 3 (Espagne)
7/71
- (F). 0040.- NEWSLETTER/CHRONIQUE ICCROM
International Center for the Study of the Pre-
servation and the Restoration of Cultural Pro-
perty. 13 via S. Michele 00153, Rome (Italie)
7/71
- (F). 0041.- STUDIES IN CONSERVATION
International Institute for Conservation of
Historic and Artistic Works. 6 Buckingham
Street. London WC2N. 6BA. GB.
7/71
- (F). 0042.- ANTIQUARIES JOURNAL
Oxford University Press, Press Road. Neasden,
London NW 10 et 200 Madison Ave. New York. N.
Y. 10016, U.S.A.
7/72
- (F). 0043.- JOURNAL OF GLASS STUDIES
Corning Museum of Glass. Corning. N.Y. 14832
U.S.A.
7/72
- (F). 0044.- LA CÉRAMIQUE MODERNE
22, rue Le Bru, 75013 Paris (France)
7/72

CLASSIFICATION THEMATIQUE

(F). 1.- GÉNÉRAL:

- 11.- Références générales de Conservation. 0001; 0002; 0003; 0004; 0005
- 12.- Ethique, Philosophie et Théorie de la Conservation. 0006; 0007
- 13.- Archéologie. 0005; 0007; 0008; 0009
- 14.- Formation des Restaurateurs. 0010; 0011

(F). 2.- TECHNIQUES DE FABRICATION:

- 21.- Développement historique des matériaux siliceux. 0012
- 22.- Techniques de fabrication. 0012; 0014
- 23.- Thèmes particuliers. 0015

(F). 3.- TECHNIQUES DE CONSERVATION:

- 31.- Altérations. 0002; 0004; 0007
- 32.- Méthodes appliquées à la Conservation des matériaux siliceux. 0002; 0004; 0007; 0016; 0017; 0018; 0019; 0020; 0021
- 33.- Conservation "in-situ". 0005; 0009; 0020
- 34.- Thèmes particuliers. 0022

(F). 4.- ANALYSES:

0023; 0024

(F). 5.- PUBLICATIONS BIBLIOGRAPHIQUES (Périodiques):

- 51.- Général: Méthodes et Techniques de Conservation. 0025
- 52.- Techniques de fabrication des matériaux siliceux. 0026

(F). 6.- PUBLICATIONS BIBLIOGRAPHIQUES (Non périodiques):

- 61.- Général: Méthodes et Techniques de Conservation. 0027
- 62.- Techniques de fabrication des matériaux siliceux. 0028
- 63.- Techniques de Conservation des matériaux siliceux. 0029; 0030; 0031; 0032
- 64.- Archéologie. 0033
- 65.- Analyses. 0034

(F). 7.- REVUE:

- 71.- De Conservation. 0035; 0036; 0037; 0038; 0039; 0040; 0041
- 72.- Autres. 0026; 0042; 0043; 0044

INDEX ALPHABETIQUE PAR AUTEURS

- (AATA) ART AND ARCHAEOLOGY TECHNICAL ABSTRACT: 0025
- ANDRE, Jean-Michel: 0016
- ANNALES DU LABORATOIRE DE RECHERCHE DES MUSÉES DE FRANCE: 0036
- ANON: 0022
- ANTIQUARIES JOURNAL: 0042
- ATKINSON, R.J.: 0008
- BECKSMANN, R.: 0029
- BLANC, A.: 0012
- BOLETIN DE LA SOCIEDAD ESPAÑOLA DE CERAMICA: 0026
- BOLLETTINO DELL 'ISTITUTO CENTRALE DEL RESTAURO: 0035
- BRANDI, Cesare.: 0006
- BRILL, R.H.: 0023
- BULLETIN DE L ' INSTITUT ROYAL DU PATRIMOINE ARTISTIQUE: 0037
- CCI: 0038
- CONSERVATION DIVISION NHPS: 0030
- CORPUS VITREARUM MEDII AEVI (CVMA): 0017
- FRODL - KRAFT, Eva.: 0013
- GAUDEL, P.: 0033
- HEDVALL, J.A; JAGITSCH, R and OLSON, G.: 0028
- HONEY, W.B.: 0015
- ICCROM - UNESCO: 0010
- ICOM - CONSERVATION COMMITTEE: 0001
- IIC - CONSERVATION IN ARCHAEOLOGY AND THE APPLIED ARTS: 0007
- INFORMES Y TRABAJOS DEL INSTITUTO DE CONSERVACION Y RESTAURACION DE OBRAS DE ARTE: 0039
- INTERNATIONAL CONFERENCE ON THE APPLICATION OF NUCLEAR METHODS IN THE FIELD OF WORKS OF ART: 0024
- JACOBI, R.: 0018
- JOURNAL OF GLASS STUDIES: 0043
- LA CERAMIQUE MODERNE: 0044
- LARNEY, J.: 0019
- NEWSLETTER/CHRONIQUE ICCROM: 0040
- NEWTON, R.G.: 0031
- PHILIPPOT, P.: 0011
- PLENDERLEITH, H.J.: 0002
- ROME CENTER: 0032
- S. MESEGUER, José.: 0020
- SAYRE, E.V.; MEYERS, P.: 0034
- SEMINARIO REGIONAL LATINOAMERICANO DE CONSERVACION Y RESTAURACION: 0003
- SINGER, F; SINGER, Sonja S.: 0014

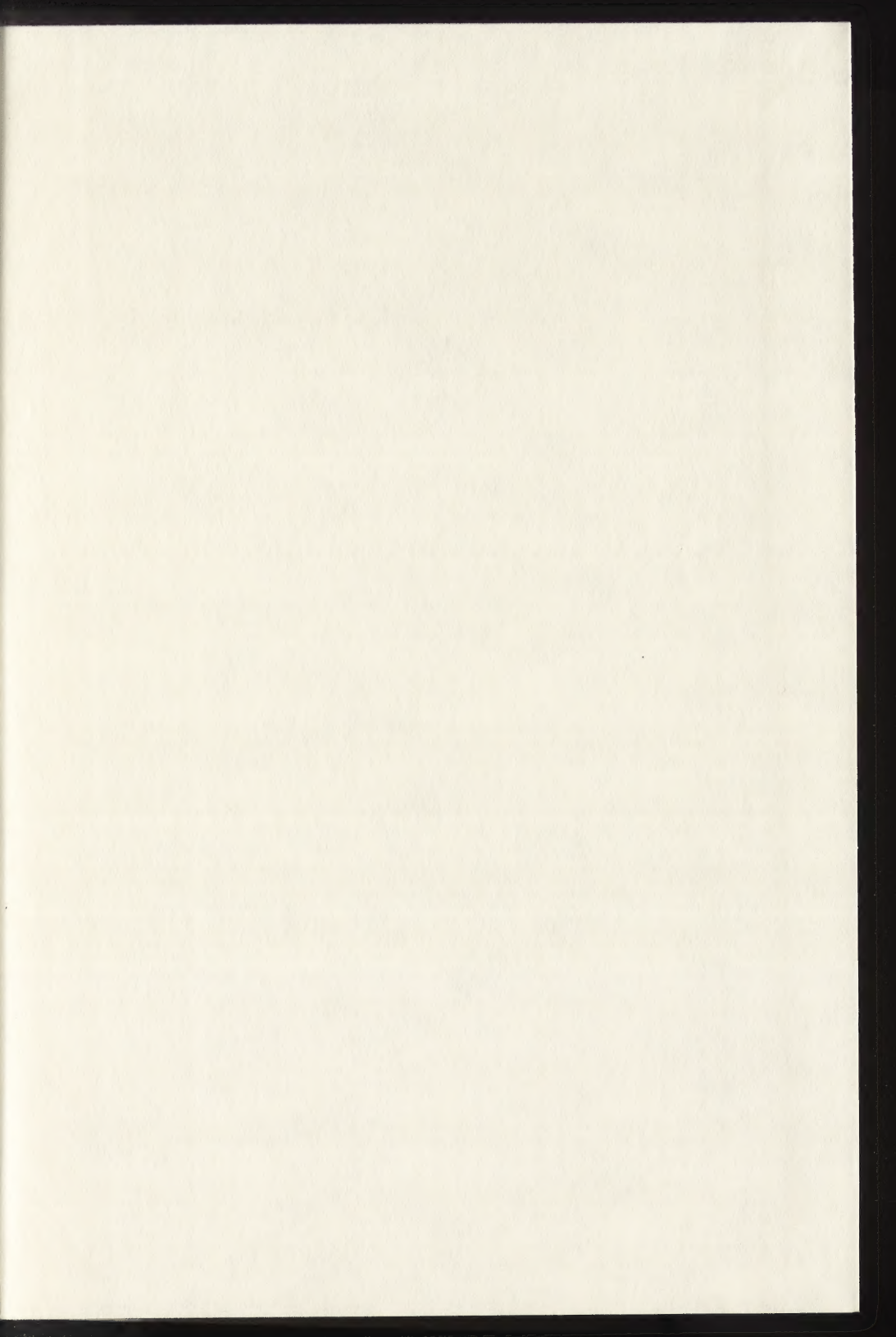
81/21/1-10

- STUDIES IN CONSERVATION: 0041
- UNESCO: 0004, 0005
- VON IMHOFF, H.C.: 0027
- WERNER, A.E.A: 0021
- WHEELER, M.: 0009

033 118318









GETTY CENTER LIBRARY

N 8554.5 I61C73 1981

v.3 c. 1

Preprints /

CONS

BKS

ICOM Committee for C



3 3125 00228 5571

